A SPECTROPHOTOMETRIC STUDY OF SOME COBALTOUS FATTY ACID SALTS AND COMPLEXES

By

JOHN C. McARTHUR
Lieutenant, U.S. Navy

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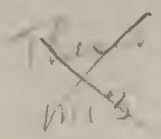

CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

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Date Professor in charge

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Head, Department of Chemistry

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John C. McArthur

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I. INTRODUCTION

The amine complexes of cobaltous salts have been extensively studied in the solid state[1] and in aqueous solutions[2], but there has been very little work done with these materials in inert solvents. Myers[3] cryoscopic work with cobaltous acetate-amine complexes in benzene and cyclohexane indicated that the maximum number of primary amine molecules to complex with cobalt (II) in these inert solvents, is four as opposed to six for the same reactants in aqueous solution. It is to be expected that marked differences such as maximum coordination number and bond type may exist between aqueous solutions and inert solutions for the following reasons. The basic nature of water causes it to compete with any ligand for coordination sites on the cobalt atom while no such competition exists in inert solvents. The high dielectric constant of water will promote the dissociation of any cobalt salt in solution, so that the effect of the complementary species in the original cobalt compound will be removed except in its capacity to compete as a base with the ligand. In inert solvents, however, dissociation will occur to a small degree or not at all, so that the acid species in solution is an entire neutral salt molecule. Finally, infrared spectral studies may be made of these complexes in certain inert solvents such as carbon tetrachloride or alkanes, while this is, of course, impossible in aqueous solutions.

An infrared study of cobalt-amine complex systems in inert solvents would be particularly desirable because of the inter-

atomic vibrational data that are potentially available. Study of the spectra of such solutions should provide the information necessary to decide the bond type, covalent or ionic, between the cobalt atom and its complement, namely an organic acid radical. The question as to this bond type was raised by Myers'[3] cryoscopic work, but the nature of the linkage has not been confirmed. Furthermore, the effect on this bond of adding ligands to the metal compound is of interest both academically and from a practical point of view. The practical viewpoint is due to the widespread use of cobaltous napthenates as drying agents in linseed oil films. The exact mechanism of this action as a drying agent is not known but has been the object of considerable interest. Myers[3] made an exhaustive search for amines to complex with manganese and other logical metals to replace cobalt compounds as dryers and found that the drying action of manganese compounds could be improved enormously by complexing with amines, but that the action of cobalt was essentially not improved by amine ligands.

This investigation was formulated on the basis of the information and ideas presented above. It was designed around the following three hypotheses: First, the infrared spectra of inert solvent solutions of a cobaltous salt of a long chain fatty acid could be interpreted so as to shed some light on the bond types present between metal and oxygen. Second, the infrared spectra of these solutions with amine ligands added in various concentrations would likewise be interpreted to give information on the formation of new metal nitrogen bonds and any

changes in the metal-oxygen bonds. Third, it would be possible to determine the maximum number of coordination sites available to amine ligands on the cobalt atom under these conditions and the order of magnitude of the successive formation constants for the complex species formed.

Cobaltous 2-ethyl hexanoate was chosen as the cobalt compound for study because of its known solubility in inert solvents and the availability of 2-ethyl hexanoic acid. Amyl amine was chosen as the complexing ligand because it was known to form complexes rapidly with cobalt (II). Carbon tetrachloride was selected as the inert solvent because of its transparency in the infrared and its availability.

As will be seen in later sections, certain difficulties were encountered, particularly in the preparation of pure cobaltous 2-ethyl hexanoate. The infrared spectra did not yield as much information as desired so the investigation was extended to include visual spectrophotometric study of carbon tetrachloride-cobaltous 2-ethyl hexanoate-amyl amine solutions.

II. PREPARATION OF COBALT (II) FATTY ACID SALTS

Preparation of a pure sample of a carbon tetrachloride soluble cobalt (II) salt turned out to be a major problem. The first preparation was attempted using the procedure of Shedlovsky and Arnold.[4] A slight excess of 2-ethyl hexanoic acid was added to an aqueous solution of sodium hydroxide, followed by several extractions with ethyl ether to remove the excess acid. The ether was completely removed by boiling the solution down to about half the original volume. This solution of sodium 2-ethyl hexanoate was then slowly added with stirring to as aqueous solution of excess cobaltous chloride.

$$2\ RCOONa + CoCl_2 \longrightarrow \underline{Co(RCOO)_2}\downarrow + 2\ NaCl$$

The above metathetical reaction apparently took place, however, the precipitated cobalt salt was a deep purple tarry mass that defied proper washing and purification in the normal manner. The preparation was repeated several times varying the relative concentrations of the two primary solutions but always with the same tarry precipitate. It was observed that the metathetical reaction was quite temperature-sensitive and, when all solutions were chilled to about 10°, no precipitate was observed upon mixing, although the color of the cobaltous chloride solution changed very slightly toward a bluish-red hue. Heating the mixture to slightly above room temperature brought about the formation of the usual precipitate. Cobaltous 2-ethyl hexanoate was found later to have a positive heat of solution, so this failure to obtain a precipitate at low temperature is understandable.

Samples of the cobaltous 2-ethyl hexanoate obtained in this

manner were found to be extremely soluble in carbon tetrachloride, toluene, benzene, and other inert solvents --- so soluble that purification by recrystallization was impossible. The concentrated solutions became syrupy and when evaporated to dryness, a tough bluish-red film formed rather than yielding any crystals. Apparently, the cobalt salt and these inert solvents are miscible in all proportions. It was also found that the tarry precipitate was quite soluble in water but the solution process was very slow at room temperature.

It was decided at this point to look for another salt of cobalt that would meet the requirements of solubility in carbon tetrachloride and be amenable to preparation in pure crystalline form. Cobaltous acetate was available but was not soluble in the solvent. Cobaltous butyrate was the logical choice.

The same general procedure was attempted for preparation of cobaltous butyrate, but in all trials a blue flocculent precipitate was formed (presumably impure cobaltous hydroxide). Attempts to extract any cobaltous butyrate from the reaction mixture with toluene or carbon tetrachloride resulted in a slight purple coloration of the extracting liquid. This gave the false impression that the butyrate was soluble in these inert solvents, so another method of preparation was attempted.

Cobaltous hydroxide was prepared by precipitation from an aqueous solution of cobaltous chloride with a slight excess of aqueous sodium hydroxide. Digestion, washing and drying gave a clean powdered pink sample. 0.032 moles of cobaltous hydroxide, 60 ml. of toluene and 0.053 moles of n-butyric acid were placed

in a refluxing apparatus and allowed to stand for one hour at room temperature. During this time, the cobaltous hydroxide turned dark purple and formed a sticky mass at the bottom of the flask while the toluene remained uncolored. Refluxing for several hours gave no coloration to the toluene. 0.18 moles of butyric acid were then added, making a total excess of about 0.17 moles; whereas originally, the cobaltous hydroxide was in excess by .0058 moles. A Stirling-Bidwell condenser was inserted in the refluxing apparatus to collect the water formed and the refluxing was continued for one hour. The solid material went into solution, the toluene became dark purple and a little over 1 ml. of water was collected in the Stirling-Bidwell condenser (theoretical water yield: 1.13 ml.). The toluene solution was transferred to a distillation apparatus. Considerable excess toluene was added (about 200 ml) and the mixture was distilled down to about 75 ml. At this point, considerable precipitate had formed and the toluene had lost its purple color and was a light yellow. Since n-butyric acid boils at 163°and toluene at 110°, a considerable amount of the excess acid was removed by this distillation. The precipitate was removed, washed with toluene and then dried in air. It was a light pink color, similar to cobaltous hydroxide or cobaltous acetate. It was characterized as cobaltous butyrate on the basis of the method of preparation, the fact that it charred in a flame, had the odor of butyric acid and the infrared spectrum of a sample pressed in a potassium bromide disk was quite similar to the spectrum of cobaltous acetate, as would be expected. It was found that

cobaltous butyrate was not soluble in toluene or carbon tetrachloride, even at their boiling points, but was soluble in water. It was found to be soluble in a mixture of butyric acid and carbon tetrachloride.

Further investigation of the butyrate, although of interest, was not made since it was not soluble in carbon tetrachloride.

Preparation of cobaltous n-caproate was next attempted with the hope that the increase in the length of the carbon chain from four in the butyrate to six in the caproate would permit solubility of the caproate in carbon tetrachloride. The caproate was prepared in the same manner as the first attempt at preparing the 2-ethyl hexanoate. A solution of the sodium n-caproate that had been extracted with ether was added to a cobaltous chloride solution. A light purplish-blue precipitate formed that had no tendency to form a tar. It was washed with water and dried over magnesium perchlorate. Unfortunately, this material was not soluble in carbon tetrachloride; however, it was soluble in a mixture of a little caproic acid and carbon tetrachloride.

The question arose at this point as to whether the 2-ethyl hexanoate was actually soluble in the inert solvents carbon tetrachloride and toluene. It had been found that neither the n-butyrate nor the n-caproate were soluble in carbon tetrachloride or toluene, but that they were soluble when the parent acid was present in solution. All preperations of the 2-ethyl hexanoate carried out had been in the presence of excess acid, hence a true solubility test had not been performed.

Preparation of a sample of cobaltous 2-ethyl hexanoate was

carried out in toluene

$$Co(OH)_2 + 2\ R\text{-}COOH \longrightarrow Co(R\ COO)_2 + 2\ H_2O$$
(excess)

in the same manner as the butyrate had been previously prepared with a Stirling-Bidwell condenser to collect the water produced by the above reaction. 0.0571 mole of cobaltous hydroxide, 0.1082 moles of 2-ethyl hexanoic acid and 150 ml of toluene were used in the preparation. Toluene was selected because of its favorable boiling point, 111° --- high enough so the water could be driven off rapidly. The reaction took place rapidly on mixing with the evolution of heat. Upon refluxing for about one and one half hours, 1.9 - 2.0 ml of water were collected (theoretical yield: 1.95 ml H_2O). The toluene solution was a deep ultramarine blue with no reddish hue as was present in all other toluene solutions of this salt prepared previously. The solution was transferred to a distilling apparatus and distilled down to about 35 ml. There was no evidence of a precipitate but the solution was quite viscous, and it was still a deep, pure blue color. This was confirmation of the solubility of cobaltous 2-ethyl hexanoate in toluene in the absence of acid. It also showed that there is a marked difference in the solutions with and without the parent acid present. In the presence of acid, the solutions are a reddish blue (purple) while in the absence of the acid they are a pure blue. This was confirmed by adding a little 2-ethyl hexanoic acid to the pure blue solution as prepared above, whereupon the reddish color appeared. Further discussion of this point will be taken up in the next chapter.

The problem of obtaining a pure sample of a carbon tetra-

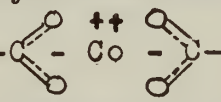
chloride soluble cobaltous fatty acid salt still remained. It was found that when a water solution of the cobaltous 2-ethyl hexanoate (prepared by metathesis in water as described before) was heated in a casserole, it changed from a red solution (appearance very similar to a cobaltous chloride solution with a blue tinge) to a cloudy blue, whereupon the familiar purple tar began to collect. When this tar was collected and removed carefully, the solution again became a clear red and a scum slowly began to form over the top. This scum had all the appearance of forming on the surface in a unimolecular film and slowly building up to visible proportions. A sizeable sample (~0.05 g) was collected for observation. It was a light blue with a very slight tinge of red and powdery when dry. It melted at a low temperature (below 100°) to give a deep blue liquid. It was suspected that this material was pure cobaltous 2-ethyl hexanoate. At the same time this scum was being prepared, it was observed that a blue-green film was forming on the bottom of the porcelain casserole. The solution was poured off, the green material scraped out carefully and dried for further observation.

Potassium bromide disks were prepared with the purple tar first formed on heating the solution, the blue scum collected, and the green material from the bottom of the casserole. The spectra obtained will be discussed in chapter five. It was concluded by comparison of these spectra with those of cobaltous acetate and other acetates as well as additional experimental data and logic, that the blue scum that forms at the water-air interface of a heated solution of the crude cobaltous 2-ethyl

hexanoate, is pure cobaltous 2-ethyl hexanoate. It was found that when the solution was made quite dilute (about 2 grams of crude salt per liter of water) no tar was formed on heating. Only the films were formed at the interfaces.

For the lack of any other suitable means of preparing the pure salt with the materials available, the tedious process of boiling a dilute solution of the crude material and collecting it with a stirring rod was used. A sample of about 0.3 grams was collected and dried over magnesium perchlorate. It was then transferred to a Abderhalden drying apparatus. The system was flushed out with prepurified nitrogen passed through barium perchlorate. Sodium hydroxide was placed in the drying pistol and the system was pumped down with an oil vacuum pump. The system was heated at the boiling point of water for 24 hours with occasional flooding with nitrogen and re-evacuation. The sodium hydroxide was then replaced with barium perchlorate and the procedure repeated for 48 hours. The system was then flooded with nitrogen, cooled to room temperature and allowed to stand for one week. The salt, when first heated, formed a deep blue melt which did not change color for the first three days. At the end of the one week standing period, the material was very dark blue, almost black, to reflected light and deep blue with a very slight reddish tinge to transmitted light. The sample was found to be quite sticky when removed from the sample tube in a dry box flooded with dry nitrogen. The sample was weighed and dissolved in carbon tetrachloride for further investigation. Unfortunately, time did not permit spectroscopic examination of this sample.

III. INTERPRETATION OF THE PROPERTIES OF THE FATTY ACID SALTS AS FOUND DURING THEIR PREPARATION

The solubility of the four fatty acid salts worked with show an interesting although inconclusive trend. All four are soluble in water; the rate of the solution process being much slower for the 2-ethyl hexanoate than for the others. The acetate, n-butyrate and n-caproate are quite insoluble in toluene or carbon tetrachloride while the addition of a 2-ethyl group to the n-caproate, giving the 2-ethyl hexanoate makes this material miscible in all proportions with these solvents. There seems to be an effect over and above that caused by the increase in the number of carbon atoms per molecule here for such a discontinuous behavior. It is quite probably the branching of the acid carbon chain at the 2-position that is responsible for this sudden change in behavior. It is shown in chapter five that the cobalt-oxygen bond is ionic in all these salts. Therefore, it is postulated that the acetate, n-butyrate, and n-caproate crystallize in some pattern that can be called an ionic lattice, while the 2-ethyl hexanoate with its 2-ethyl side chain sterically interfering with the ionic center  , is forced to exist an a molecular crystal in the solid state. The solubility in water is accomplished in the normal way for the first three compounds --- water acting as a dielectric medium splitting up the ionic crystal lattice, while at the same time, the Co^{++} ions are being solvated to form $Co(H_2O)_6^{++}$. The 2-ethyl hexanoate, however, is resistant to attack by water because van der Waals' forces bind the neutral $(RCOO)^-Co^{++}(OOCR)$

units together into a molecular crystal lattice, and a high dielectric medium such as water is not effective in separating these neutral units. Slow solvation by water does occur because the surface molecules are attacked slowly, forming the hydrated $Co(H_2O)_6^{++}$ species which is apparently thermodynamically more stable than the unsolvated 2-ethyl hexanoate. Solubility in an inert solvent, however, proceeds by a different mechanism. In general, if the internal pressure, $\frac{\partial E}{\partial V}$, of solute and solvent are appreciably different, solubility will be quite low. It can be readily appreciated that a material that forms an ionic crystal lattice will have higher internal pressure than one which forms a molecular crystal because of the weak van der Waals' forces binding the neutral units together in the latter. Therefore, the postulate that the 2-ethyl group essentially masks the polar center of a molecule of cobaltous 2-ethyl hexanoate from the surrounding molecules of the same material and causes it to act much as a hydrocarbon in its solubility in inert solvents is consistent with observed facts. Likewise, the extremely slow but considerable solubility of this compound in water is explained by this hypothesis.

It is possible, of course, that the increase in size of the organic radical in going from n-caproate to 2-ethyl hexanoate is responsible for the sudden change in solubility characteristics, but this seems unlikely. The solubility of the cobaltous salts of n-caprylic acid and 2-ethyl butyric acid should verify or disprove the postulated role of the 2-ethyl group.

The matter of the decrease in solubility of cobaltous 2-ethyl hexanoate in water upon heating is easy to explain. Anhydrous cobaltous chloride is a deep blue while the hydrated material is red and gives a red aqueous solution at room temperature. Heating the solution causes a slight shift in the color toward the blue; hence, the dehyrated species becomes more stable with an increase in temperature. Heating a solution of the 2-ethyl hexanoate, which is stable only because of the energy of hydration of the cation, causes the cation to dehydrate and combine with the 2-ethyl hexanoate anion present. In short, the heat of solution of cobalt 2-ethyl hexanoate in water is positive.

The interesting phenomenon observed on heating an aqueous solution of cobaltous 2-ethyl hexanoate requires explanation. As mentioned in the last section, heating of such a solution in a porcelain casserole was attended by clouding of the solution and a change in overall color from red to purplish. This was followed by formation of a purple tar, clearing of the solution to give the original red solution (only more dilute) and subsequent formation of a blue scum on the surface as the solution boiled. A blue-green film also formed on the bottom of the casserole. The purple tar was identical in appearance to the original salt prepared by metathesis and its infrared spectrum (KBr disk) was almost identical with that of a carbon tetrachloride solution of the original salt. The infrared spectrum of the blue scum formed on the surface showed a carboxylate infrared absorption peak almost identical with that of cobaltous

acetate and showed no absorption peak attributable to water. The blue-green substance showed an infrared absorption spectrum almost identical to that of the blue compound, except that it showed a definite water absorption peak. (A more detailed discussion of the infrared absorption of these and other compounds and solutions will be given in chapter five.)

Disregarding the purple tar for the time being; there appears to be the following situation. At the water-air interface $Co(RCOO)_2$ is formed, while at the water-porcelain interface $Co(RCOO)_2 \cdot x\, H_2O$ is formed. A quite plausible explanation is that at the water-air interface the $R\,COO^-$ groups arrange themselves with the $(COO)^-$ downward toward the water, and with the R tails upward. Immediately under this layer would be a layer of hydrated cobaltous ions to preserve electrical neutrality. As a cobaltous ion loses its water of hydration --- presumably by some statistical process, a $(RCOO)^- Co^{++} -(OOCR)$ molecule would form and lie out flat on the surface --- on top of the monomolecular layer of "R tails". This essentially isolates the newly formed molecule from the bulk of the system. The two $R\,COO^-$ groups removed from the surface layer are quickly replaced by two others from the body of the solution. As this process continues, the tendency toward upward orientation of the R-tails becomes even stronger, since there soon is an interface that is essentially water-hydrocarbon instead of water-air.

It was observed that when the solution was dilute enough, no tar was formed in the body of the solution --- only the blue scum formed on the surface (and the blue-green material on the

porcelain.) This observation is quite compatible with the proposed surface formation mechanism, and is indeed to be expected. Dehydration of cobaltous ions is by no means complete at 100°, consequently a finite solubility of the salt in water at this temperature is expected since precipitation was supposed to occur as a result of dehydration. The oriented concentration at the surface is much greater than in the bulk. In addition, a molecule is elevated out of the solution at the surface as soon as it is formed, preventing re-equilibration with the solution as takes place in the bulk. Consequently, a formation of the solid phase occurs on the surface at a much lower gross concentration than necessary for formation in the bulk.

The details of a mechanism to explain the formation of a solid hydrate at the water-porcelain interface seem less clear, but the following is proposed as a possibility. The R COO^- groups would be expected to orient with the polar end toward the porcelain in view of the known acidic nature of a porcelain surface. The R-tails certainly have no desire to orient into the water but neither do they have any attraction for the porcelain, but given the attraction between the COO^- and the porcelain, the R-tails would then tend to group together as tightly as possible. This would be achieved by orientation into the solution, ideally perpendicular to the porcelain surface for a unimolecular film. A layer of hydrated cobaltous ions would back up this layer to preserve electrical neutrality. As a neutral molecule of $(RCOO)^-$ Co^{++} $^-(OOC\ R)$ is formed in this matrix, it cannot be elevated out of the reaction site to a neutral climate, as was postulated for

the water-air interface. If it is ejected into the bulk of the solution, it is free to redissolve since the bulk of the solution is not saturated. Since the formation of a compound at this interface is observed it must be concluded that the neutral molecule does remain near the reaction site. Being held at this interface, it is subject to different chemical forces than it would be in the bulk of the solution.

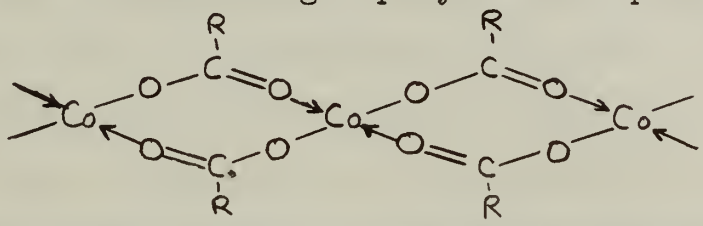
Now to consider the purple tar that has been the unwelcome product of all attempts to prepare cobaltous 2-ethyl hexanoate in an aqueous media. Almost conclusive proof that it is a mixture of complexed and uncomplexed species of the cobaltous salt was provided by two simple experiments. When a carbon tetrachloride solution of the material was heated, it changed from a reddish-blue or purple to a pure deep blue solution and the original purple color was regenerated when the solution cooled. The temperature range considered was from about 20° to 50° C. This is certainly the behavior that could be expected from a loosely complexed cobaltous salt because it is well known that these complexes become increasingly unstable as the temperature is raised. Furthermore, heating a sample of the material on a spatula caused it to melt and bubble for a short time, obviously losing some volatile material. The bubbling ceased after a short time and the liquid showed a marked tendency to wet the metal spatula by creeping up at an angle of at least 45°. When a carbon tetrachloride solution of the cooled melt was made, it was found to have the same pure blue color, when at room temperature, as did the heated solution of the original purple tar.

Heating the solution to boiling had no effect on the hue or intensity of the color. The obvious conclusion is that the cobaltous 2-ethyl hexanoate in the purple tar is at least partially in the form of what is commonly referred to as a normal complex[5]. (Normal complexes are those which can reversibly dissociate in solution into their components, while penetration complexes cannot reversibly dissociate in solution.) A study of the infrared spectrum as discussed in chapter five shows that the complexing ligand must be 2-ethyl hexanoic acid. Therefore, it must be concluded that there is an average of much less than one acid molecule coordinated per cobalt atom since the only source of the free acid in water solution of sodium 2-ethyl hexanoate is that produced by hydrolysis. Extensive hydrolysis and removal of the free acid by complexing would make the solutions quite basic, and since, in all cases, excess cobaltous chloride was used, no appreciable concentration of hydroxide ions could exist without precipitation of the quite insoluble cobaltous hydroxide. There was no evidence of cobaltous hydroxide precipitation, even on long standing.

In an inert solvent such as a carbon tetrachloride where the potential ligand does not have to compete with the solvent for the metal atom, it is to be expected that some ligands will show fairly strong complexing tendencies, whereas they show little or no such tendencies in a aqueous solution. Indeed, it may be predicted as a general rule that a series of ligands will act as stronger bases toward a particular metal atom in an inert solvent than they will in comparable situations in aqueous solu-

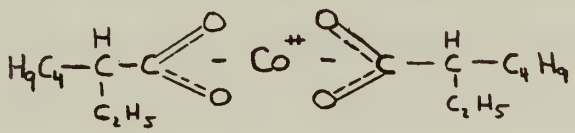
tions. No reference could be found to neutral carboxylic acid molecules complexing with metals in aqueous solutions, but this seems to definitely be the case here.

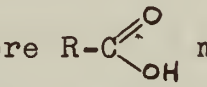
The idea of the complex present in the purple tar carbon tetrachloride solutions being a polynuclear species such as



is ruled out since the complex was apparently destroyed when volatile material was removed from the tar by heating. This does not rule out the independent existence of the above polynuclear species completely, but it makes it quite unlikely because of the color stability, with respect to heating, of a solution of the tar that had been "decomplexed" by heating.

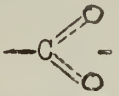
From the evidence available, it is most likely that the species present in the pure blue solutions is:



and that in the purple solutions one or more  molecules are loosely coordinated to some cobalt atoms through the C = O group of the acid.

An interesting sidelight on the chemistry of this purple tarry form of cobaltous 2-ethyl hexanoate is the phenomenon observed when it is pyrolyzed in a casserole. It first melts and bubbles as mentioned before, but when heated on the full flame of a ring burner, it soon begins to char and smoke and a silvery

metallic-looking, transparent film is deposited on the upper part of the walls of the casserole. This film conducts electricity although it shows quite high resistance --- but this is to be expected from an extremely thin coating of metal. The possibility that this film is an oxide of Co (III) is not completely ruled out, but from the appearance of the film, it was deposited from the gaseous state and, if this is true, the oxide is definitely ruled out. It would not be an oxide of Co (II) because this would be soluble in aqueous ammonia and the film was not soluble.

The most promising explanation is that a volatile cobalt carbonyl was formed during the pyrolysis and that it subsequently decomposed on contact with the hot casserole walls to give a deposit of cobalt metal. Pyrolysis of an organic compound with insufficient bound oxygen and a poor external oxygen supply ordinarily gives considerable carbon monoxide in the products. These conditions are met in this compound and the reduction of the Co (II) to Co° can be visualized as an electron transfer from the  group directly to the metal atom, or as a more complex process of reduction, through free radicals of the type R•. Many other metal reduction processes can be conceived but this would be pure speculation without further experimental evidence.

It is known that cobalt carbonyls can be prepared by the action of carbon monoxide on cobalt compounds with highly polarizable non-metals such as sulfur and iodine. This suggests reduction of the cobalt ion by direct transfer of electrons from the organic acid anion seem like a reasonable possibility in the

case under discussion.

An interesting physical property of the purple cobalt 2-ethyl hexanoate should be mentioned here in the closing of this section. It was found that a freshly precipitated batch could be formed into a ball easily and the material acted very much like "silicone bouncing putty". The ball of material bounced from a hard surface with no gross deformation yet could be kneaded slowly into any shape desired. When an attempt was made to shape the material by a rapid motion of any sort, it shattered into a great number of pieces. A cone of the material collapsed into a shapeless mass in the bottom of a beaker on standing overnight.

A detailed study of this phenomenon is beyond the scope of this work. However, the observations are strong evidence for the existence of cobalt 2-ethyl hexanoate in either an amorphous or molecular crystalline form rather than in an ionic crystal lattice.

IV. THEORETICAL ASPECTS OF INFRARED ABSORPTION SPECTRA

In the region of the infrared spectrum between 2 and 15 microns, the absorption peaks observed are quite characteristic of specific molecular linkages, and pretty much independent of other atoms that may be associated with these linkages[6]. For example, an -OH group in an organic molecule will absorb almost exactly the same characteristic wave length of infrared energy regardless of whether it is attached to a methyl, ethyl or even a tertiary butyl group. Slight differences in the wave length of energy absorbed are observed, but in general, the absorption band for a particular linkage lies within a narrow range of frequencies. These absorption bands are not monochromatic, but are usually quite sharp as contrasted to the absorption bands in the visible and ultraviolet range.

A molecular linkage, such as O-H can be visualized as an undamped harmonic oscillator composed of two masses, the oxygen atom and the hydrogen atom, and a joining spring ---------- the energy of the bond between the two. The solution for the equation of motion for such an oscillator is:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (1)$$

where ν = wave number = cm^{-1}

k = force constant of bond = dynes/cm

μ = reduced mass = $\dfrac{m_O\, m_H}{m_O + m_H}$

Now the energy associated with this oscillator is by wave mechanics:

$$E = (v + \tfrac{1}{2})\, hc\nu \qquad (2)$$

where E = energy

v = vibrational quantum number = 0,1,2,···

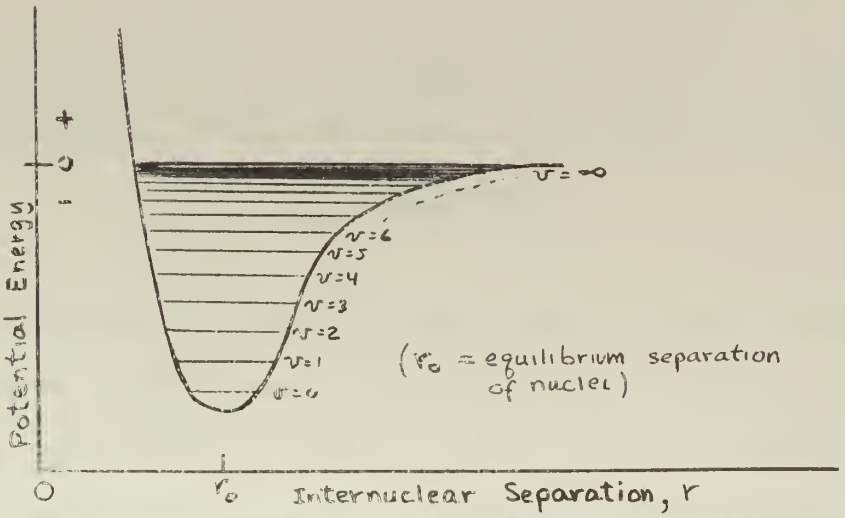
h = Planck's constant

c = velocity of light

This assumes that the restoring force constant of the bond is truly a constant but this is not entirely true. There is a gradual weakening of the force constant k with increasing separation of the two atoms of the vibrator that is expressed by a subtractive term in the energy expression as shown below. x is called the anharmonicity constant.

$$E = (v + \tfrac{1}{2})hc\nu - (v + \tfrac{1}{2})^2 hcx\nu \qquad (3)$$

The diagram of a typical potential energy curve for a diatomic molecule as shown below makes it clear why such an anharmonicity term is necessary. Similar higher order terms, to express more exactly the deviation of a real molecule from a true harmonic oscillator, can be added but they serve no useful purpose in this argument.

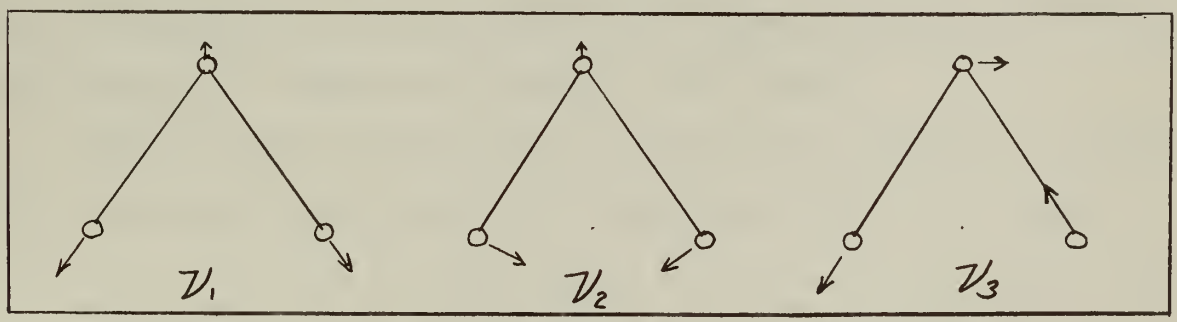


Typical diatomic molecule potential energy curve

FIGURE 1.

Since k is very nearly a constant near the bottom of the potential energy well shown in figure 1, the spacing between the allowed energy levels near the ground state is almost exactly E as defined by equation (2). Consequently, electromagnetic energy of the frequency corresponding to E will be absorbed and scattered by the molecular oscillator. It should be noted that such an oscillator, both in theory and practice, will display absorbance in the infrared only if the oscillator has a dipole moment.

Up to now only a diatomic oscillator has been considered. The basic concepts discussed can be extended in theory to polyatomic molecules for which comparable mechanical ocsillators can be constructed. The diatomic oscillator has only one vibration mode, but a nonlinear triatomic molecule has three fundamental vibration modes as depicted in figure 2.



Fundamental Vibration Modes For a Triatomic Molecule

FIGURE 2.

The three modes of vibration have three separate characteristics frequencies as defined by appropriate wave equations. Extension to larger molecules is obvious and it can be appreciated that the vibrational pattern of even a triatomic molecule is quite com-

plex. A simple triatomic molecule such as H_2O shows seventeen absorption bands[8] including the fundamentals shown above, combination bands equal to the sums and differences of fundamental frequencies and the harmonics which result from a vibrational quantum jump of 2 or more instead of 1 as observed with the fundamental frequencies. It might be anticipated that there would be enough coupling between the various vibrational modes to render the absorption spectrum unrecognizable on the basis of such a simple theory, but fortunately this is not the case.

As suggested previously, a particular bond vibration and hence absorption frequency, can be defined approximately in terms of a characteristic force constant or vibration frequency for that bond, regardless of its surroundings. This force constant must be defined as a range of values to allow for the small dependence on environment that is observed. It is this small dependence on environment that makes a study of the infrared spectra of complexes useful in this work.

Environmental differences in the force constant or vibration frequency for a particular bond arise from two primary sources. The state of aggregation of the molecules under consideration affects the nature of the absorption band. In the gaseous state, the molecules are, in general, independent of interactions with each other, While in a condensed state or in a solution, interactions of several types can arise causing broadening of the absorption bands and small shifts in the peak absorption frequencies. Table 1 shows the shift in fundamental absorption band frequencies for water in its three states of

aggregation[9].

State	ν_1	ν_2	ν_3
gas	3650 cm^{-1}	1595 cm^{-1}	3755 cm^{-1}
liquid	3448	1642	3397
solid	3156	1644	3259

Fundamental Absorption Bands for Water

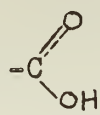
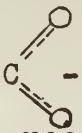
TABLE 1.

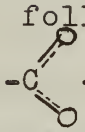
The second environmental factor affecting the force constant is the nature of the remainder of the molecule of which the bond under consideration is a part. Table 2 shows the average wave number of the absorption peak for the C = O in a variety of different types of compounds.[7]

Compound Type	Carbonyl Absorption Peak Wave Number (cm^{-1})
R-CO-H	1780
R-CO-R	1710
R-CO-OH	1656
R-CO-NH_2	1662
R-CO-OR	1735
R-CO-Cl	1792
R-CO-O^-	1565

Carbonyl Absorption Peaks

TABLE 2.

The groups  (I), and  -(II) are of particular interest this work. As seen in the proceeding table, the wave number,

and hence the force constant for the carbonyl group in (I), is higher than that in (II). This follows from the fact that (II) can be represented in the form  , as an average of two canonical forms with essentially a three halves bond between each equivalent carbon-oxygen. Such a 3/2 bond will be weaker than the pure double bond of (I) and, consequently, the force constant of the latter is the largest.

In general, any molecular arrangement that tends to fix the -C = O in a non-resonating structure will make the force constant of the bond higher than it is for the carboxylate ion. This argument has been used to determine whether the bonding between a carboxyl group and a metal is covalent or ionic[10a] since covalent bonding will prevent resonance in the carboxyl group while purely ionic bonding will not.

V. INTERPRETATION OF THE INFRARED SPECTRA

A model 21 Perkin-Elmer double beam infrared spectrophotometer was used to obtain the spectra of several solids and solutions. The solids were pressed into potassium bromide disks and a pure potassium bromide disk was used in the reference beam. The solutions were all in carbon tetrachloride and carbon tetrachloride was used in the reference beam of the instrument.

Absorption bands with peaks between 1545 cm^{-1} and 1570 cm^{-1} were found for solid samples of calcium acetate, mercuric acetate, cobaltous acetate, cobaltous butyrate and cobaltous 2-ethyl hexanoate (see spectra 1 and through 5). A carbon tetrachloride solution of 2-ethyl hexanoate (spectrum 6) also showed an absorption band in this range. Since the observed absorption peaks between 1545 cm^{-1} and 1570 cm^{-1} are assignable to the carboxylate ion,* these spectra were considered as proof that the metal to oxygen bonds in cobaltous 2-ethyl hexanoate are ionic.

Since cobaltous 2-ethyl hexanoate is an ionic compound, solvation in inert solvents will yield neutral ion triplets $(RCOO)^{-}\ Co^{++}\ (\bar{O}OCR)$. These ion triplets will be referred to as molecules hereafter, and the solid cobaltous 2-ethyl hexanoate will be referred to as existing in molecular crystals.

It was pointed out in chapter two that when cobaltous 2-ethyl hexanoate was prepared by metathesis and subsequently treated with water, three different compounds were obtained. In chapter three an interpretation of this phenomenon was given but the strongest evidence for showing the composition of these

*See Table 2

three compounds was left to this chapter. Infrared spectra number 3a, 3b, 3c, are for the originally precipitated purple cobaltous 2-ethyl hexanoate, the blue material formed on the surface of a boiling aqueous solution of the latter, and the green material formed on the bottom of the casserole, respectively. Spectra 3b and 3c show that the carboxylate absorption bands for the blue and green material are essentially the same as those observed for the butyrate and acetates (see spectra 1, 2, 4, and 5), except that the absorption peaks in spectra 3b and 3c are about 25 cm^{-1} lower. Spectrum 3c shows a fairly strong absorption peak at 3340 cm^{-1} which is definitely attributable to water, while 3b shows only a broad weak absorption at this wave number. These observations comfirm the idea presented in chapter three that the blue compound (3b) formed on the surface of a boiling solution is cobaltous 2-ethyl hexanoate while the green material (3c) is cobaltous 2-ethyl hexanoate with water coordinated to the cobaltous ion. The conclusion that the green compound is hydrated and the blue compound dehydrated is further strengthened by their colors. Cobaltous salts invariably show a shift in color from blue toward red when they are hydrated. Compounds such as cobaltous acetate and cobaltous chloride change from a deep blue violet to light pink, and deep blue to red, respectively, when hydrated. The change in color observed with the compounds under study are in the right direction for the assumptions made about their composition. It is not particularly disturbing that the color shift is not as great as observed with other salts since we are comparing molecular crystals with

ionic crystals. Since it is shown in chapter six that the complex of cobalt 2-ethyl hexanoate with one amyl amine ligand is green, it is proposed that the green compound discussed above is the monohydrate of cobaltous 2-ethyl hexanoate.

Spectrum 3a for the purple cobaltous 2-ethyl hexanoate shows a broader carboxyl ion absorption band than 3b or 3c , with the peak shifted about 25 cm^{-1} toward higher frequencies. Also, a peak is present in 3a at 1680 cm^{-1} which is not observed in 3b or 3c . This is assigned to the carboxyl group of 2-ethyl hexanoic acid. Spectrum 14 for 2-ethyl hexanoic acid in carbon tetrachloride shows a carboxyl absorption peak at 1710 cm^{-1}. The shift of this peak to 1680 cm^{-1} in 3a is what would be expected if the oxygen of the acid carboxyl group was coordinated with the cobaltous ion, since the C = O force constant would be weakened slightly. Coordination of an organic acid ligand onto cobalt in cobaltous 2-ethyl hexanoate would be expected to change the positions occupied by the carboxyl ions relative to each other and cause a certain amount of interaction between the two carboxyl ions and the carboxyl group of the ligand. This would cause broadening of the carboxyl absorption bands as observed in spectrum 3a . On the basis of the foregoing, it is concluded that spectrum 3a is the sum of the spectra of uncomplexed cobaltous 2-ethyl hexanoate, and this species complexed with one molecule of 2-ethyl hexanoic acid.

It was desirable in working with solutions of cobaltous salts, to keep the concentration of the salt as low as possible to keep intermolecular effects to a minimum. The more dilute

the solution, the longer must be the light path through the solution. The liquid cells available for the spectrophotometer are not designed for easy variance of the light path. They are constructed of two flat sodium chloride plates separated by an amalgamated lead spacer and bolted together in a steel frame. The thickness of this lead spacer determines the length of the light path. For this work, the cells were assembled with three amalgamated lead spacers, 0.1 millimeter thick each, providing a total light path of 0.3 mm. Each disassembly of these cells to change the spacers puts the sodium chloride plates in grave danger of being cracked, so the light path was not changed after the initial setting.

The spectra of the carbon tetrachloride solutions are not too satisfactory for detailed interpretation because the absorption of infrared energy is not great enough to fully develop the absorption bands. The carboxylate absorption peak could be brought down to about 30% transmission instead of the 70% or 80% obtained with no loss of accuracy. This would provide considerably more detail in the remainder of the spectra.

A set of solutions of cobaltous 2-ethyl hexanoate (the purple variety made by metathesis in water) and amyl amine was prepared in carbon tetrachloride in a dry box under an atmosphere of dry air. The compositions of the solutions were calculated on a basis of the cobaltous 2-ethyl hexanoate being 95% pure (probably a little low) and the amyl amine being 100% pure. The solutions made were as shown on the following page in Table 3.

Spectrum and solution number	Concentration of amyl amine	Concentration of cobaltous 2-ethyl hexanoate
6	0	0.01 M
7	.0025 M	0.01 M
8	.005 M	0.01 M
9	.010 M	0.01 M
10	.025 M	0.01 M
11	.050 M	0.01 M
12	.100 M	0.01 M

Composition of Solutions
TABLE 3.

The colors of the solutions changed from reddish blue, through green to red with increasing amine concentration. This was taken as conclusive evidence that the amine was complexed with the cobalt. Visual spectra were taken for these solutions and they will be discussed in chapter six.

The spectra of these solutions were taken on a model 21 Perkin-Elmer Spectrophotometer, using the liquid sample cells referred to previously. Carbon tetrachloride was used in the reference beam in all cases.

The carboxylate absorption band is very similar for all these solutions and, since the spectrum are not fully developed, it is difficult to draw firm conclusions from them. One observation worthy of comment is the variance in the extinction coefficient of the carboxyl ion peak. Solution number six, with no amyl amine, shows a peak transmission of 68%. Stepping through the solutions in numerical order toward higher concentration of amyl amine, it is seen that transmission at the frequency of this peak increases to a maximum of 78% in solution 9 and then decreases back to 69% for solution 12. As will be shown in chapter six, this fall and rise of transmittance can be

correlated with the build up and decay of the monoamine complex species. Therefore, the complex species with one amyl amine ligand bonded to the cobalt ion has a lower extinction coefficient at the carboxylate vibration frequency than do either the uncomplexed metal salt or the complex species with two amine ligands. An explanation for this change in extinction coefficient based on the symmetry of the complex molecule is postulated in the next paragraph.

The most stable configuration of the neutral cobaltous 2-ethyl hexanoate molecule in solution is that in which the two carboxyl ions are located in diametrically opposite positions across the cobalt ion with the two  planes normal to each other. With this geometry, there is a minimum of mutual interference between the carboxyl ions. When a single ligand is introduced into the coordination sphere of the cobalt ion, the geometric symmetry will be upset with a resultant increase in mutual interference between the carboxyl ions. It is this mutual interference that is postulated to give rise to the decrease in absorbance by the carboxyl ions in the first complexed species. The original symmetry between the carboxyl ions will be restored when another amine ligand enters the coordination sphere since it will presumably occupy a position 180° from the first ligand. This restoration of symmetry will decrease the mutual interference between carboxyl ions with a concomitant increase in absorbance. The third and fourth ligands will probably each enter positions on a plane normal to a line passing through the two carboxyl ions and containing the first two ligands. There-

fore, the introduction of the third and fourth ligands should not cause any interference between the carboxyl ions or decrease in absorbance.

No appreciable frequency shift was observed in the carboxyl absorption band as amyl amine concentration was increased from zero to 0.1 M in the 0.01 M cobalt 2-ethyl hexanoate solutions. Therefore, it must be concluded that the cobalt to oxygen bonds remain ionic when the amyl amine ligands coordinate with the cobalt.

It was not possible to follow any shifts in the amine group absorption bands since the only band attributable to the amine group appeared very weakly between 1500 and 1650 cm^{-1} and was masked by the carboxyl absorption band.

It did not seem possible to deduce anything firm about the successive formation constants or the maximum coordination number for this system from the infrared data obtained, so it was decided to obtain visual spectra of the solution described in Table 3. These visual spectra are discussed in the next chapter.

VI. INTERPRETATION OF THE VISIBLE SPECTRA

The visible spectra of the carbon tetrachloride solutions of cobaltous 2-ethyl hexanoate and amyl amine listed in Table 4 were taken on a Beckman DU Spectrophotometer with a Spectrocord automatic scanning and recording device. These spectra are shown in Appendix I (spectra 15 through 21).

Spectrum number	Concentration of amyl amine	Concentration of cobaltous 2-ethyl hexanoate
15	0	0.01 M
16	.001 M	0.01 M
17	.0025 M	0.01 M
18	.005 M	0.01 M
19	.010 M	0.01 M
20	.025 M	0.01 M
21	.050 M	0.01 M

Composition of Solutions
TABLE 4.

Since there was considerable variance between the individual spectra, it appeared that they would be useful in determining the successive formation constants* that describe the equilibrium between the various complex species present in solution. Direct calculation of formation constants in this case was highly impractical, if not impossible. The best approach to this problem appeared to be the often used technique of setting forth an hypothesis and then testing it with the experimental data. The hypothesis will be set forth in the following paragraphs.

The theoretical calculation of the successive formation

*For an explanation of the terms: formation constant, formation curve, $\bar{n}$, and degree of formation, see Appendix II.

constants for an ideal complex system is based completely on statistics. It is assumed that the tendency of any species in a series M, MA, MA_2 ------ MA_N to add one more ligand is proportional to the number of unoccupied coordination sites. Conversely, the tendency for a particular species to lose a ligand is directly proportional to the number attached. From these two assumptions, Bjerrum[2] shows that the n^{th} formation constant is defined by:

$$k_n = \frac{(N-n+1)(n+1)}{(N-n)n} k_{n+1} \qquad (4)$$

where N is the maximum coordination number

and $$k_n = \frac{[MA_n]}{[MA_{n-1}][A]} \qquad (5)$$

rewriting (4) gives

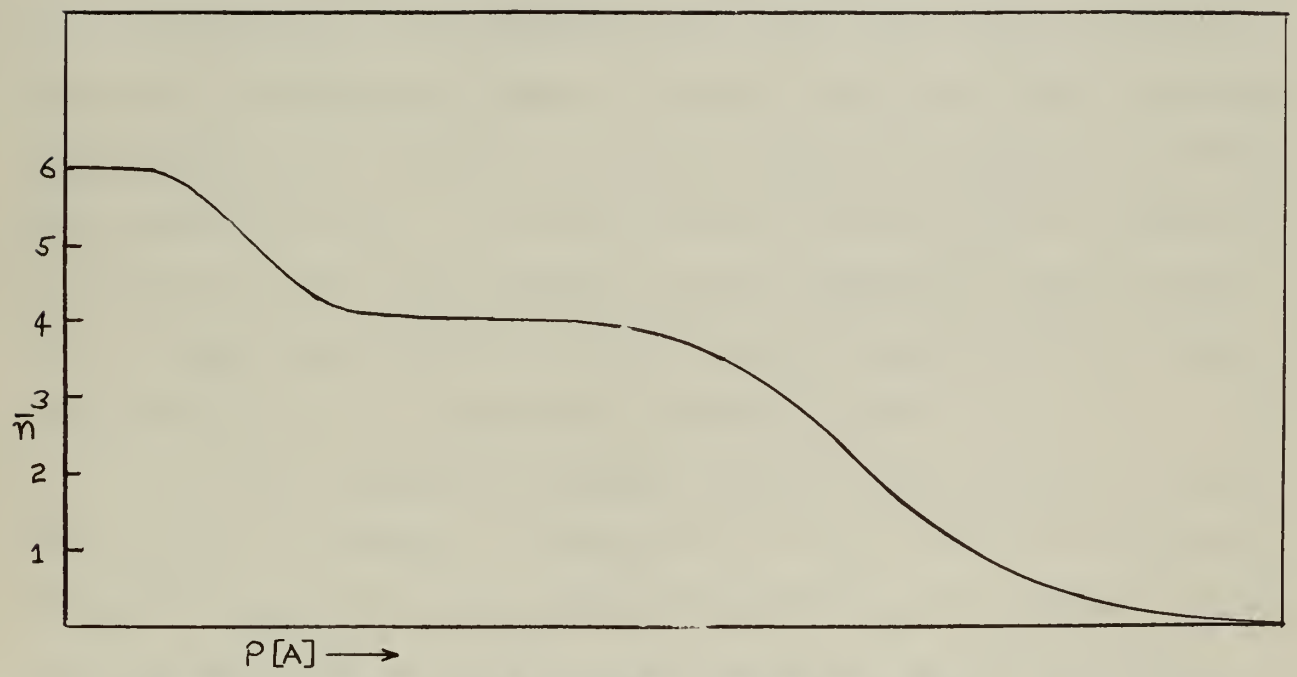
$$k_{n+1} = \frac{(N-n)n}{(N-n+1)(n+1)} k_n \qquad (6)$$

From equation (6) the last N-1 formation constants can be calculated if the value of k_1 is known.

It could not be expected that such a simple approach to the calculation of formation constants would yield values in complete agreement with real systems --- indeed, it does not. The fact remains that the general trend predicted by the statistical approach is often followed in real systems closely enough so that it is convenient to define the systems in terms of its deviation from this statistical scheme. For the lack of a more suitable hypothesis of workable proportions, it was decided to use the hypothesis that the successive formation constants are

related statistically. It was necessary to select a value of N on which to base the calculation of the formation constants. Since Myers[3] showed that the maximum number of coordination positions available to amines on cobalt (II) is four in a benzene - cobaltous acetate-amyl amine system, the value of four was used in the calculations. In addition, the values of $\bar{n}$ versus free amine concentration obtained by Myers in the above mentioned system were plotted as a segment of a formation curve, and the criterion was established for the selection of k_1 that the formation curve resulting from this selection should fit Myers' segment of a formation curve as closely as possible.

The reasoning used in selecting the value of k_1 needs some explanation. Bjerrum[2] shows that if N = 6 and k_5 and k_6 are very much smaller than the first four constants, the system can be treated as two separate systems --- the first with N = 4 and the second with N = 2. A formation curve for such a system is shown in Figure 3. This situation may very well apply to the system under investigation. It has been shown previously that the organic carboxylate group is ionically bound to the cobalt and, consequently, the 3d orbitals of the cobalt are not appreciably disturbed by the presence of the two 2-ethyl hexanoate ions. These anions will be held quite tightly by electrostatic attraction, however, and their presence will greatly hinder, if not prevent, the coordination of the 5th and 6th ligands. The net effect of this hinderance is to make the last two formation constants, k_5 and k_6, extremely small or zero. (This leads to a question as to whether N for cobalt in such a system should be



Formation curve for a complex system with N=6. k_1, k_2, k_3, and k_4 have the theoretical statistical values. k_5 and k_6 are very small compared to their theoretical statistical values.

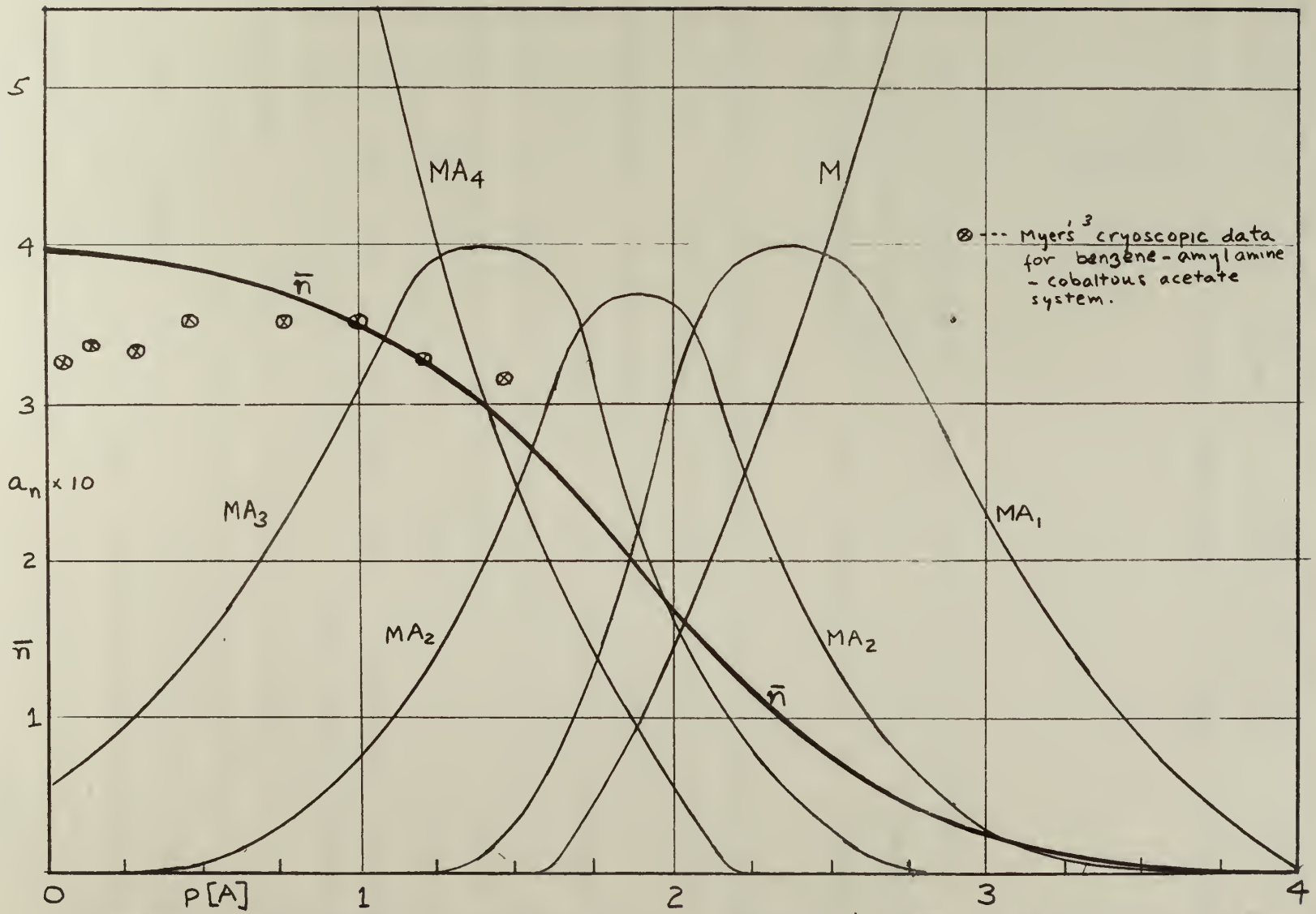
FIGURE 3.

called 4 or 6. If k_5 and k_6 are truly zero, N = 4 seems appropriate; but if these constants have any other value, no matter how small, N = 6 seems more appropriate. This is a semantic point, however, and since Myers showed that only four amine ligands would coordinate to cobalt in inert solvent solutions of higher amine concentration than used in this work, the most convenient designation, N = 4, will be used.)

Since the 2-ethyl hexanoate ions are not disturbing the cobalt 3d orbitals, it is expected that the first amine ligand to enter the coordination sphere of cobalt will do so with a driving force comparable to that of the same ligand attacking an unfettered cobaltous ion. It follows, then, that the first formation constant for the carbon tetrachloride - cobaltous 2-ethyl hexanoate - amyl amine system should be larger than the first formation constant for a comparable aqueous system.

The first formation constant for the aqueous system cobaltous chloride - ammonia is given as $k_1 = 97.8$ at 30° by Bjerrum. Bailar[10b] shows that the coordinating ability of a primary amine is less than that of ammonia. This decrease in coordinating ability is probably more than compensated for in an inert solvent system by the lack of solvent molecules competing for the coordination sites on the metal. Values of k_1 ranging from 100 to 500 were selected arbitrarily and formation curves calculated therefrom. $k_1 = 300$ produced a formation curve that best fit Myers data so this was chosen as the value to represent the system under investigation.

Figure 4 shows the formation curve and degree of formation



Degree of formation of complex species for statistical case with $k_1 = 300$ and $N = 4$

Figure 4.

of the species M, MA_1, MA_2, MA_3, and MA_4 for the statistical case based on $k_1 = 300$. The degree of formation of each individual species was calculated from the equation (7) as given by Bjerrum.[2]

$$a_n = \frac{K_n[A]^n}{1 + \sum_{n=1}^{N} K_n[A]^n}$$

where $K_n = \prod_{n=1}^{n} k_n$

A test of the validity of these hypothetical successive formation constants was make by applying a modified Jobs method of continuous variations [10c] to the visible spectra 15 through 21.

The method of continuous variations is used to test for the formation of a complex by two components in a series of solutions by plotting the absorbance observed at a certain wave length of light minus that calculated for additivity of absorbance for the two components, against the mole fraction of one of the components. The sum of the molarity of the two components is kept constant in the series of solutions, so if no complex is formed, the curve will be a straight line --- the slope depending on the relative extinction coefficients of the two components at the wave length of light used. However, if a complex is formed and its extinction differs from that of one of the prime components of the system, the curve will deviate from linearity and show a maximum deviation at the mole fraction corresponding to the composition of the complex.

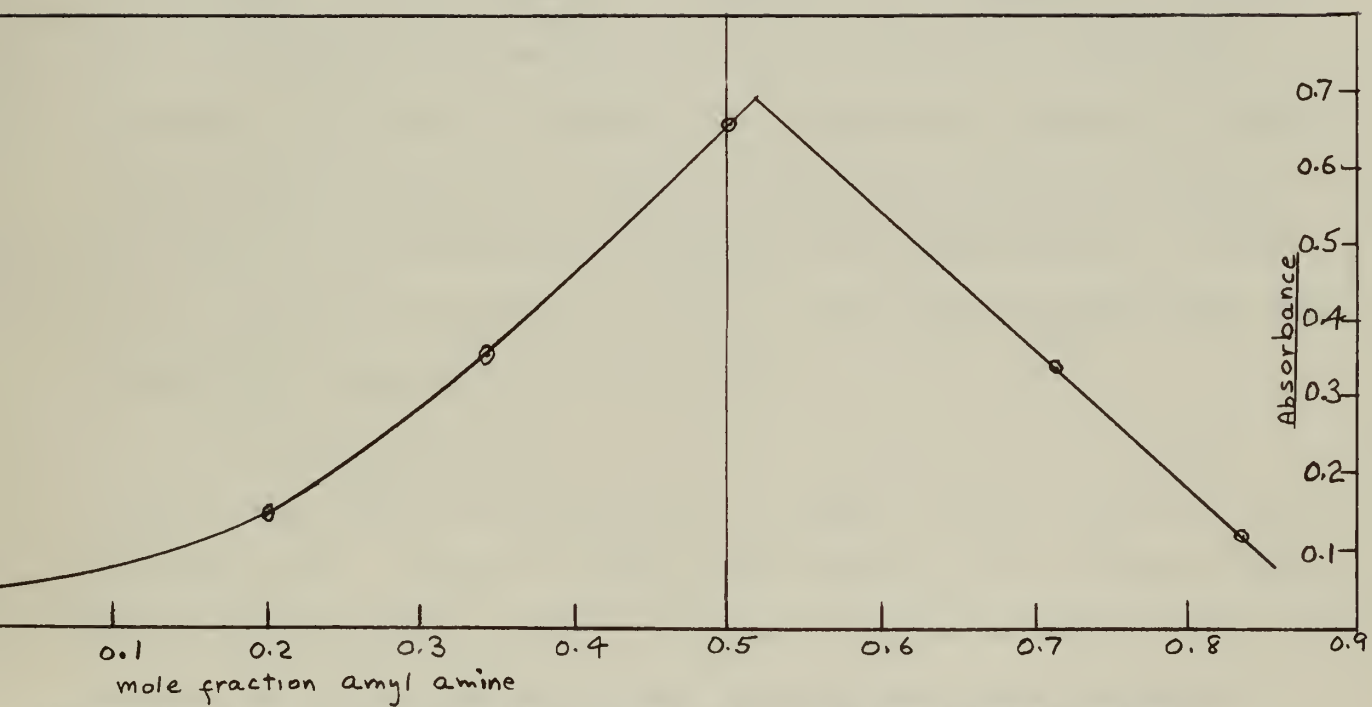
$$A + B \longrightarrow AB \qquad (8)$$

$$K = \frac{[AB]}{[A][B]} \qquad (9)$$

If the equilibrium constant in equation (9) is large, the maximum deviation from linearity in the absorbance versus mole fraction curve will be a sharp break --- essentially the intersection of two straight lines. If K is small, however, only a gradual change in slope will occur, but, in any event, there will be a maximum in deviation from linearity for this curve at the mole fraction corresponding to the composition of the complex.

A modification of the method of continuous variations was used in this system. The concentration of cobaltous 2-ethyl hexanoate was kept constant throughout the series of solutions examined and the amyl amine concentration was varied. If a complex MA_1 is formed which absorbs light of a wave length not absorbed by any other species in solution, a plot of absorbance versus total concentration of amyl amine will show the relative concentration of this species. Furthermore, if the formation constants of the system are of the same order of magnitude, as calculated earlier by the statistical method, the absorbance versus amine concentration at this wave length will show a maximum near the amyl amine mole ratio corrpesonding to the composition of the complex MA_1, i.e. 0.5.

Figure 5 is a plot of absorbance at 700 mμ by the series of carbon tetrachloride solutions shown in Table 4 in which cobaltous 2-ethyl hexanoate was kept constant at 0.01 M and amyl amine was varied from 0.001 M to 0.05 M. The nearly linear rise and fall of absorbance from near zero to 0.67 and back to near zero, as amine concentration is increased, and the sharp peak at a mole fraction of near 0.5, is good evidence that this absorb-



Absorbance at 700 mμ by solutions of 0.01M cobaltous 2-ethyl hexanoate in carbon tetrachloride with various concentrations of amyl amine.

FIGURE 5.

ance curve actually represents the relative degree of formation on the monoammine complex species.

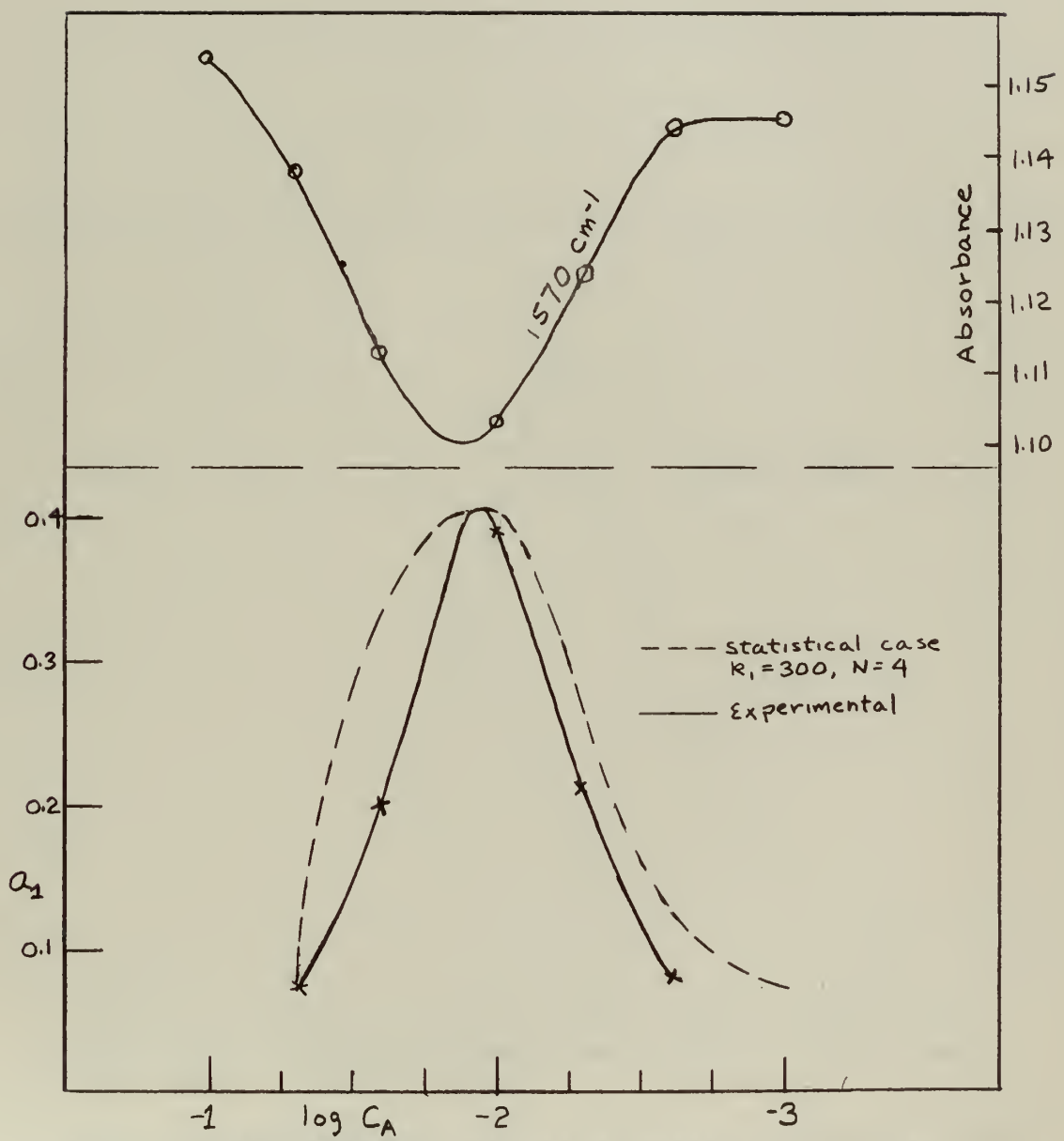
The hypothesis that the first formation constant for the system is about 300 and that the other constants follow statistically from this, can be tested by comparing the degree of formation curve of MA_1 as predicted by this treatment with the relative degree of formation of MA_1 as found experimentally from the 700 mμ visible spectra. Figure 6 is a comparative plot of the two degree of formation curves for the first complexed species. In order to transfer the statistical degree of formation curve for MA_1 from Figure 4, where the abscissa is $p[A]$, the log of the reciprocal of free amine concentration, to Figure 6, where the abscissa is log C_A, the log of total amine concentration, equation (10) was used.

$$C_A = \bar{n}\,(C_M) + [A] \qquad (10)$$

(C_M) is the molar concentration of cobalt 2-ethyl hexanoate, .01 in this case. Values of $p[A]$ were selected, the corresponding $\bar{n}$ read from Figure 4, and C_A calculated with equation (10). A series of such conputations and appropriate log conversions yielded a curve of C_A versus $p[A]$. The values of $p[A]$ corresponding to the known values of C_A for each solution were then read from this curve.

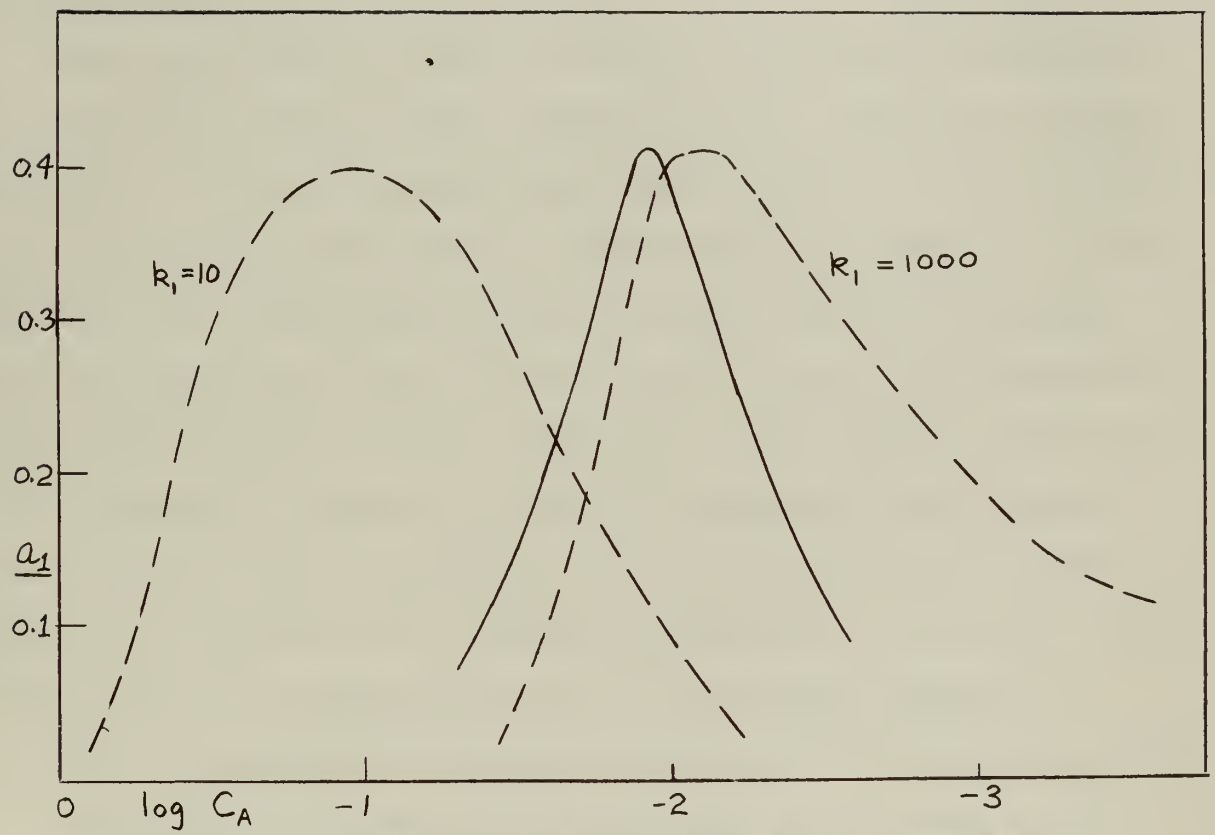
Comparison of the two lower curves in Figure 6 shows that MA_1 builds up and decays with increasing amyl amine concentration in very nearly the manner predicted by the statistical treatment with $k_1 = 300$.

Figure 7 shows that values of k_1 much smaller or larger



Build up and decay of MA_1 as a function of total amine concentration.

FIGURE 6.



Degree of formation of mono-amyl amine complex of cobaltous 2-ethyl hexanoate as a function of total amyl amine concentration.

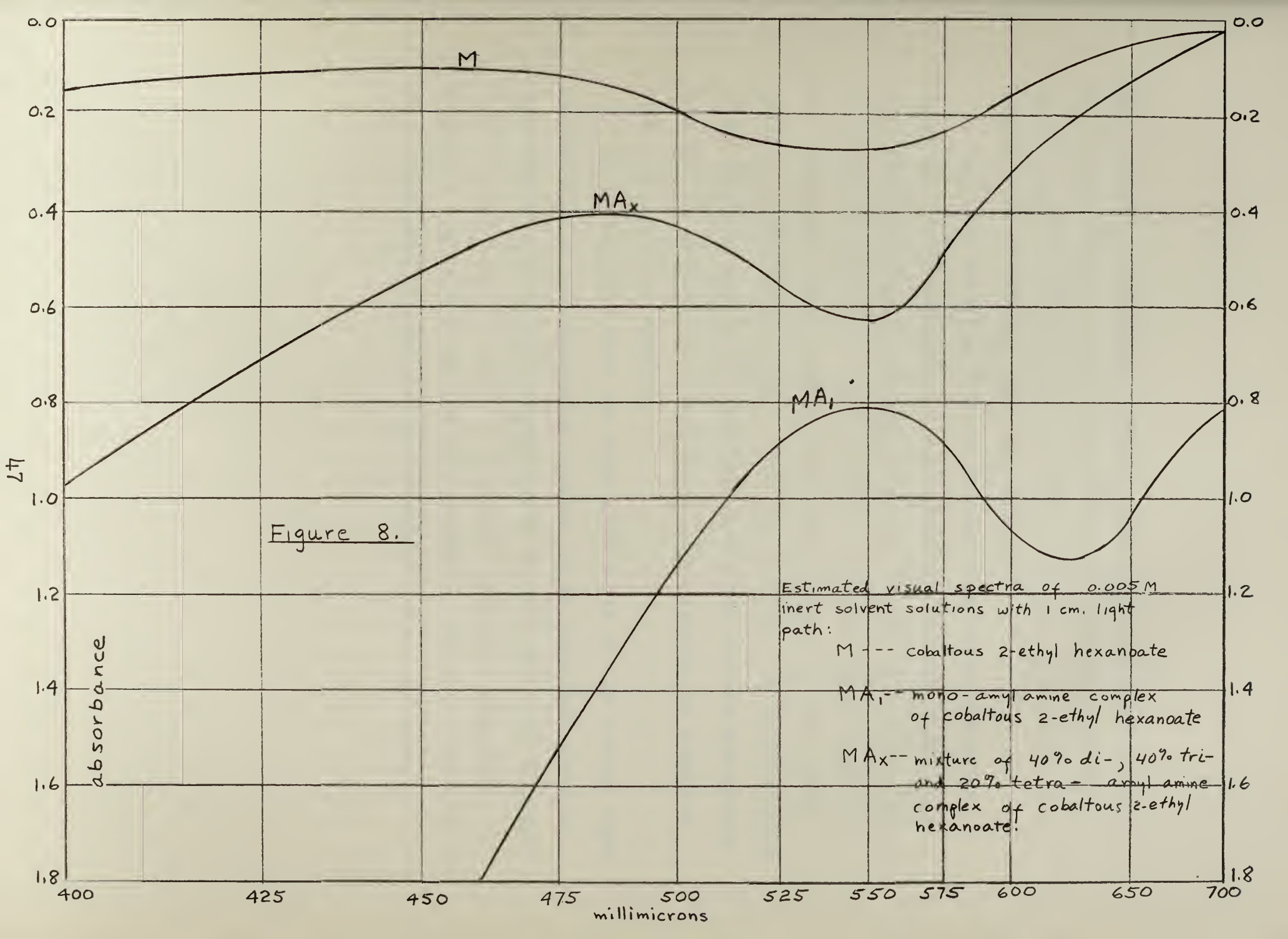
— — — Statistical case, N=4, k_1 as shown in figure
———— Experimental

FIGURE 7.

than 300 yield statistical degree of formation curves for MA_1 that deviate appreciably from the experimentally determined curve. Therefore, it can be concluded that $k_1 \cong 300$ and that k_2 has a value near 112 as predicted by the statistical treatment. Nothing can be said about k_3 or k_4 since the rise and decay of MA_2, or succeeding complex species, was not followed experimentally.

The absorbance of infrared energy at 1570 cm^{-1} (carboxyl ion vibration) by the carbon tetrachloride - cobaltous 2-ethyl hexanoate - amyl amine solutions shown in Table 3 were plotted against the log of amyl amine concentration in figure 6. The fall and rise of absorbance follows quite closely the experimentally determined build up and decay of the of the monoammine complex of cobaltous 2-ethyl hexanoate, also shown on Figure 6. It is concluded, therefore, that the mono-amyl amine complex of cobaltous 2-ethyl hexanoate has a lower extinction coefficient at the carboxyl ion vibration frequency of 1570 cm^{-1} than does either the uncomplexed salt or the diamine complex.

From the knowledge gained by analysis of the visual spectra of carbon tetrachloride - cobaltous 2-ethyl hexanoate - amyl amine solutions in the preceeding paragraphs, it is possible to estimate the visual spectra of the monoamine complex and a mixture of the more highly complexed species. Such an estimate is shown in Figure 8. The curves represent the estimated absorbance in a one centimeter cell of 0.005 molar solutions of cobaltous 2-ethyl hexanoate, the mono-amyl amine complex of this salt and a mixture of more highly complexed species of approxi-


M
MAx
MA1
Figure 8.
Estimated visual spectra of 0.005 M inert solvent solutions with 1 cm. light path:
M --- cobaltous 2-ethyl hexanoate
MA1 -- mono-amyl amine complex of cobaltous 2-ethyl hexanoate
MAx -- mixture of 40% di-, 40% tri- and 20% tetra- amyl amine complex of cobaltous 2-ethyl hexanoate.
absorbance
millimicrons
400
425
450
475
500
525
550
575
600
650
700
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8

mate composition 40% MA_2, 40% MA_3, 20% MA_4 with total molarity of .005 in cobalt. Statistical values of formation constants k_3 and k_4, following from $k_1 = 300$, were used to estimate the composition of the MA_2, MA_3, MA_4 mixture.

One very striking fact is obvious from these estimated spectra --- the monoammine complex absorbs visible light much more strongly than the uncomplexed salt or any of the more highly complexed species. In particular, MA_1 absorbs strongly in the low energy region between 600 and 700 mμ where the other species absorb only feebly. This is, of course, a manifestation of the relative ease and frequency with which certain electronic transitions are made in the monocomplexed species as compared with all the other species.

It is believed that the high absorbance of low energy light exclusively by the monoammine complex is an important observation that should be investigated further. It may very well have a direct bearing on Myers[3] finding that monoamine manganous complexes are better linseed oil oxidation catalysts than either the uncomplexed manganous salt or higher amine complexes.

VII. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

The following is a summary of the important observations and conclusions resulting from this investigation.

(a) The metal to oxygen bonds in cobaltous fatty acid salts are ionic.

(b) Coordination of amyl amine to cobalt in cobaltous 2-ethyl hexanoate does not noticeably change the ionic character of the metal to oxygen bonds. This conclusion can probably be extended to include monodendate amine ligands and cobaltous fatty acid salts in general.

(c) carboxylic acids can coordinate through their carbonyl oxygen to cobalt in cobaltous fatty acid salts.

(d) Cobaltous 2-ethyl hexanoate exists in the solid state as an aggregate of neutral ion triplets held together by van der Waals' forces rather than in an ionic lattice.

(e) Cobaltous 2-ethyl hexanoate forms a green complex with water that can be obtained in the solid state.

(f) The first formation constant for the amyl amine - cobaltous 2-ethyl hexanoate complex system, in an inert solvent, is about 300. The second formation constant has a value of about 112 as predicted by Bjerrum's statistical method. These formation constants are about three times as large as those for the aqueous cobaltous chloride - ammonia system.

(g) The relative concentration of the mono-amyl amine complex of cobaltous 2-ethyl hexanoate in an inert solvent can be determined by visual (700 $m\mu$), or infrared (1570 cm^{-1}) spectrophotometry.

(h) In an inert solvent, the extinction coefficient for the mono-amyl amine complex of cobaltous 2-ethyl hexanoate at 1570 cm^{-1} (carboxylate ion vibration) is lower than it is for the uncomplexed salt or the poly-amyl amine complexes.

(i) In an inert solvent, the mono-amyl amine complex of cobaltous 2-ethyl hexanoate has a higher extinction coefficient throughout the visible region than do either the uncomplexed salt or the poly-amyl amine complexes. Appreciable absorption of the low energy red light is exhibited exclusively by the mono-amyl amine complex.

It was not possible to determine the maximum number of coordination sites available to amyl amine on cobaltous 2-ethyl hexanoate in this investigation. However, it is felt that this goal can be achieved by additional work with visual spectrophotometry. It has been shown that the visual spectra of the species M, and MA_4, and a mixture of the remaining species vary tremendously --- an ideal situation for spectrophotometry. Application of a high speed digital computer, such as the Royal - McBee LPG - 30, would make the analysis of a large volume of spectral data practical and would provide the means for determining all the parameters necessary to describe this complex system.

It is the opinion of the author that further infrared investigations of this cobalt - amine system should be deferred until the formation parameters of the system are determined by visual spectrophotometry. With an exact knowledge of the composition of solutions, it may then be possible to interpret infrared spectra to provide additional information on the bonding and structure of the complexes.

It is recommended that solutions of cobaltous 2-ethyl hexanoate be prepared by reacting excess cobaltous hydroxide and 2-ethyl hexanoic acid, both as pure as possible, in the solvent in which it is desired to obtain the solution. Collection of the water produced by the reaction in a Stirling-Bidwell Condenser will provide a direct means of determining the end point of the reaction. Careful removal of the excess cobaltous hydroxide and dilution of the solution to a known volume would probably obviate

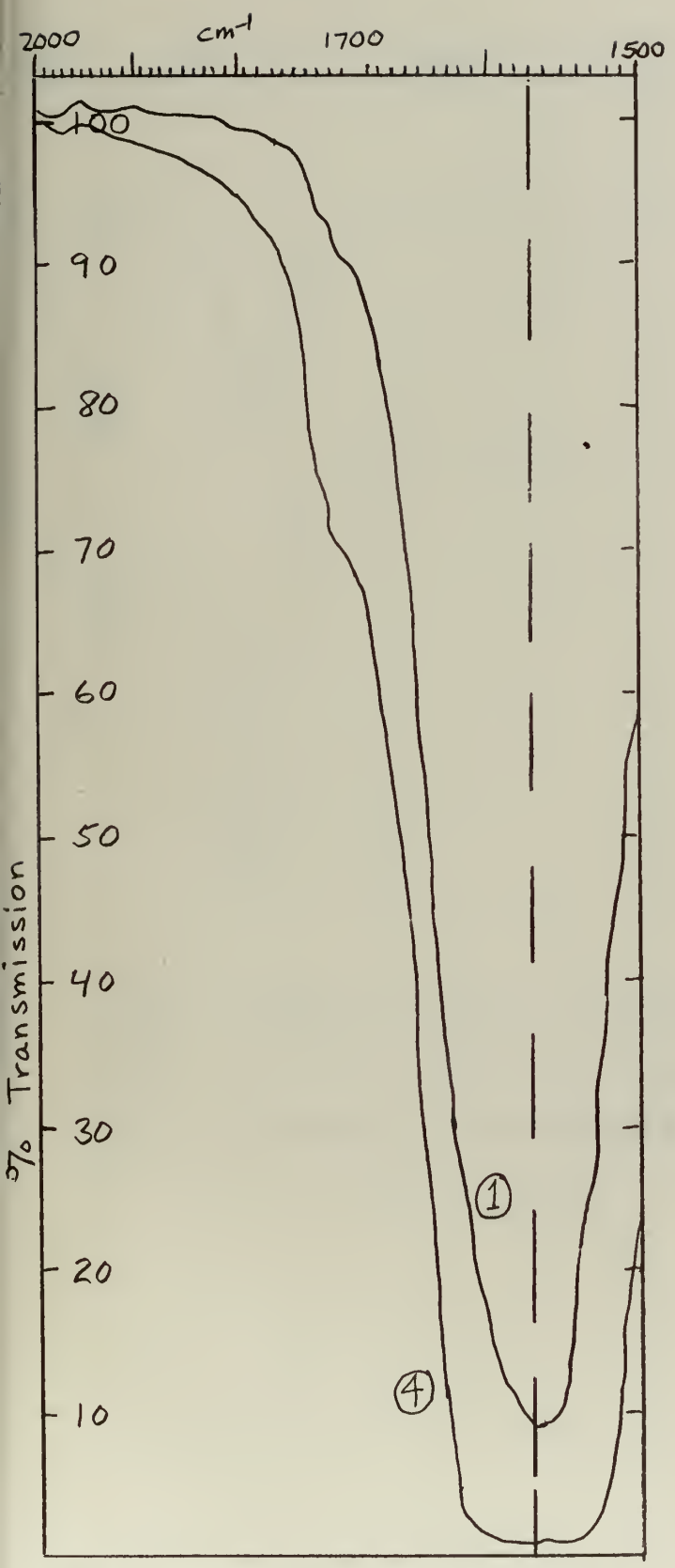
the need for an analysis of the final solution. An aliphatic hydrocarbon with a boiling point of about 120 - 150° appears to be the best choice of inert solvent from all standpoints. Such a solvent is transparent in the infrared region of interest, uniformly transparent in the visible, as inert toward the complex system as any solvent, mobile enough for easy handling, and has a high enough boiling point to permit rapid removal of water during the preparation of soluble salts.

Extension of this study to other metals and ligands would, of course, be desirable and seems practical from the results of this investigation.

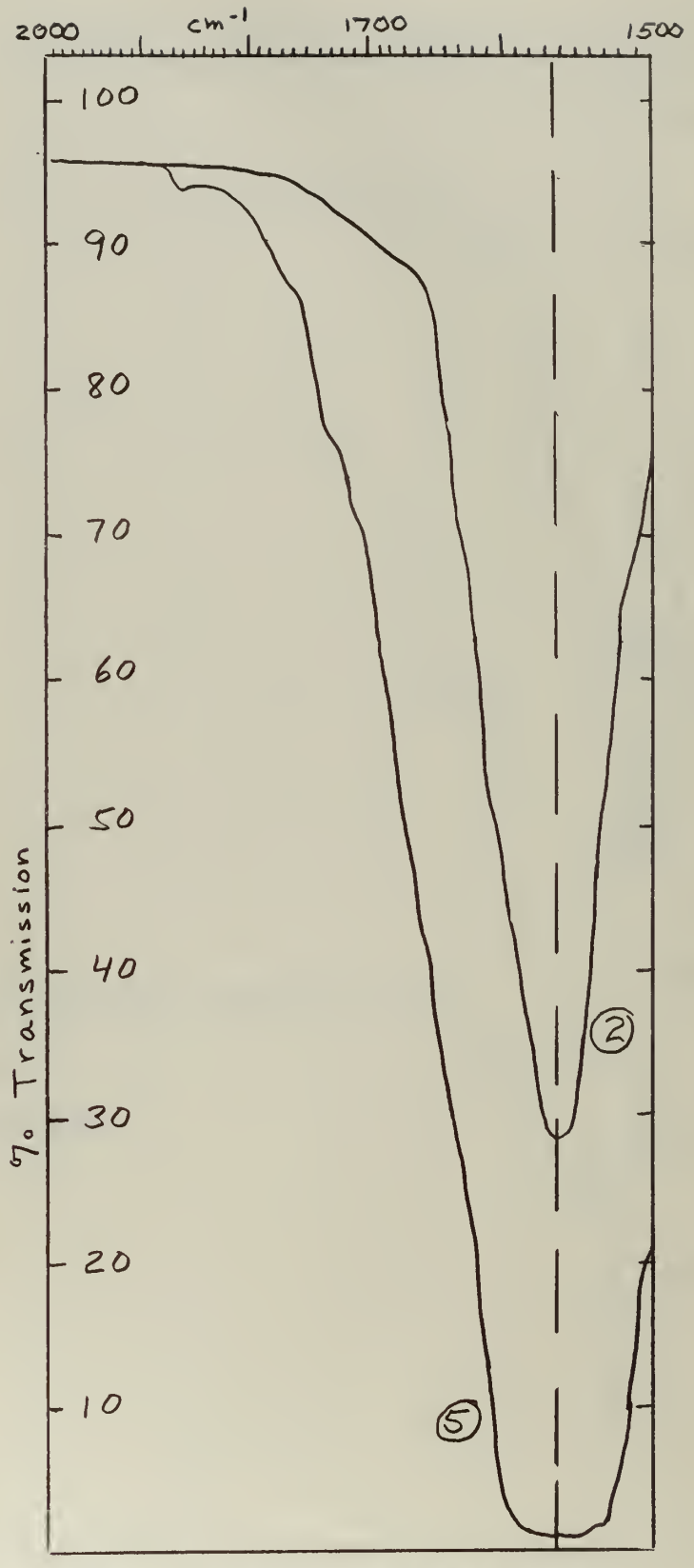
APPENDIX I INFRARED AND VISUAL SPECTRA

The infrared spectra were taken on a model 21 double beam Perkin-Elmer Spectrophotometer. A pure potassium bromide disk was used in the reference beam in conjunction with samples pressed into potassium bromide disks. Carbon tetrachloride was used in the reference beam with carbon tetrachloride solution samples. All spectra were taken with sodium chloride optics in the spectrophotometer and with the following operational settings: resolution, 927; response, 1; gain, 5; suppression, 5.

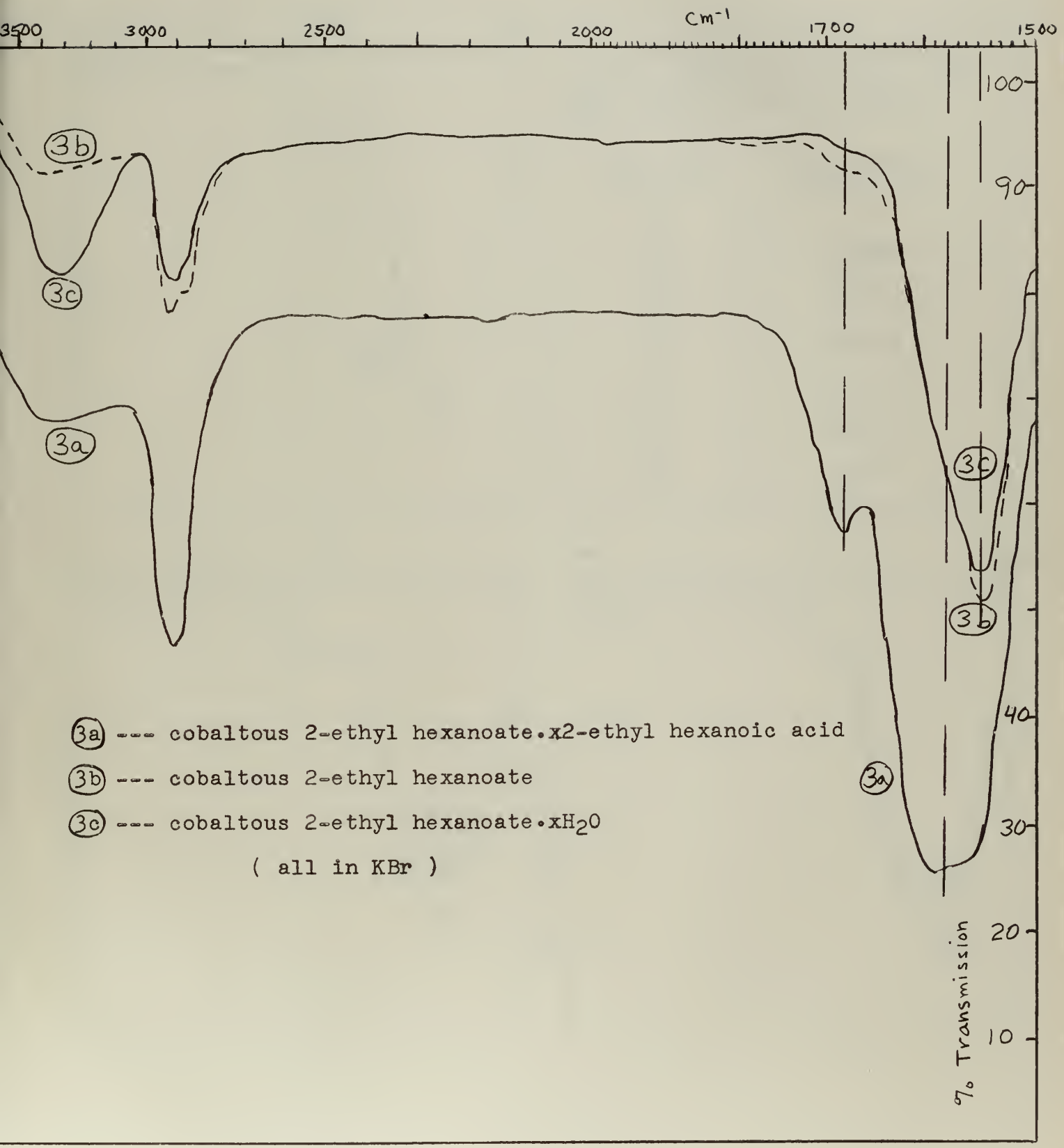
The visual spectra were taken on a model DU Beckman Spectrophotometer with a Spectrocord automatic recording attachment. Carbon tetrachloride was used in the reference beam and all spectra were taken at a speed setting of 4.

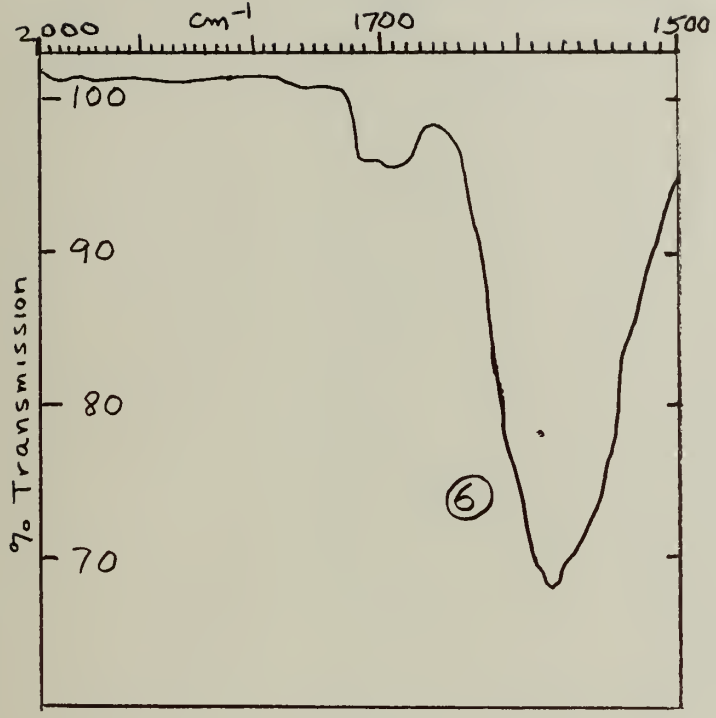


① --- cobaltous acetate in KBr
④ --- calcium acetate in KBr



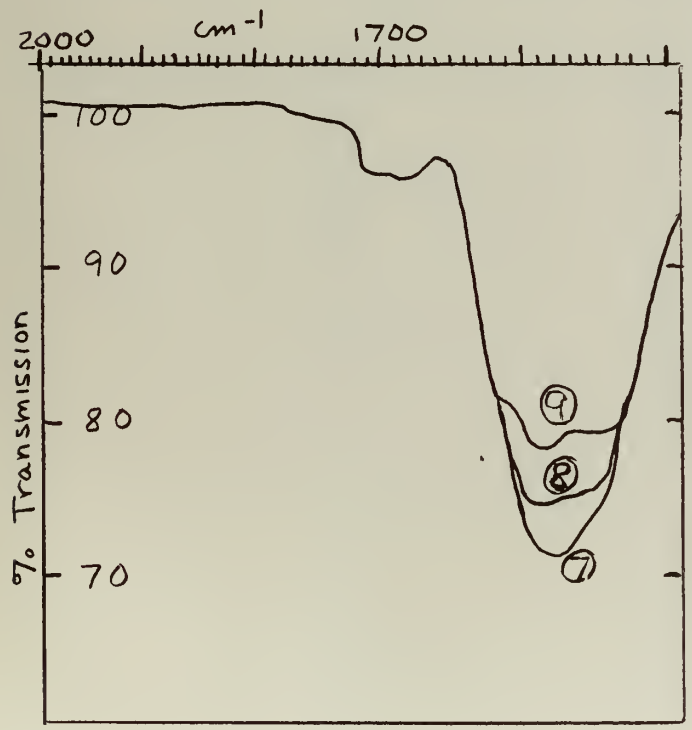
② --- cobaltous acetate in KBr
⑤ --- mecuric acetate in KBr

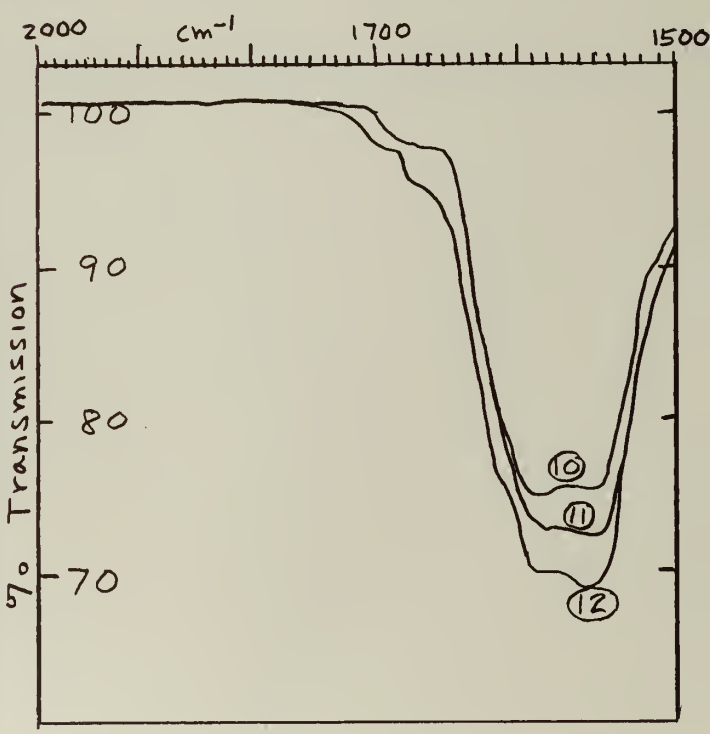

3500
3000
2500
2000
Cm-1
1700
1500
100
90
40
30
20
10
% Transmission
3b
3c
3a
3a --- cobaltous 2-ethyl hexanoate•x2-ethyl hexanoic acid
3b --- cobaltous 2-ethyl hexanoate
3c --- cobaltous 2-ethyl hexanoate•xH2O
(all in KBr)

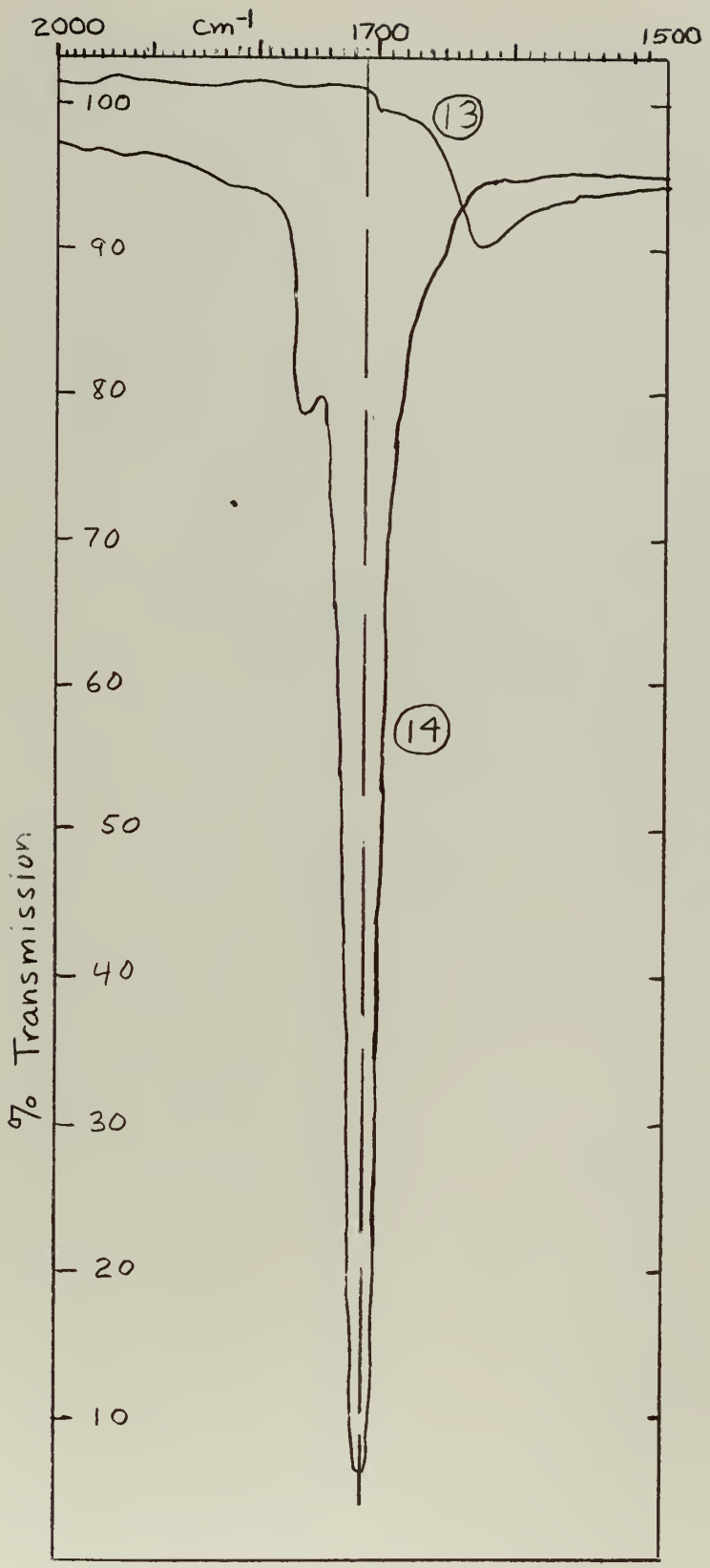


All spectra for .01M cobaltous 2-ethyl hexanoate in CCl_4 with amyl amine concentrations as shown below.

Spectrum		amyl amine
⑥	-----	0
⑦	-----	.0025M
⑧	-----	.005 M
⑨	-----	.010 M
⑩	-----	.025 M
⑪	-----	.050 M
⑫	-----	.100 M







(13) --- 0.1 M amyl amine in CCl_4

(14) --- 0.1 M 2-ethyl hexanoic acid in CCl_4

SAMPLE
SOLVENT
CONC.
CELL

SPECTRACORD
WARREN ELECTRONICS INC.

SERIAL NO.
SLIT
SCANNING TIME
DATE

VIS. 3996

All spectra for .01 M cobaltous 2-ethyl hexanoate in CCl_4 with a amyl amine concentrations as shown below.

spectrum	amyl amine
15	0
16	.001 M
17	.0025 M
18	.005 M
19	.010 M
20	.025 M
21	.050 M

ABSORBANCE

0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0

350 360 370 380 390 400 425 450 475 500 525 550 575 600 650 700 750

WAVELENGTH MILLIMICRONS

SAMPLE
SOLVENT
CONC.
CELL

SPECTRACORD
WARREN ELECTRONICS INC.

SERIAL NO.
SLIT
SCANNING TIME
DATE

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All spectra for .01 M cobaltous 2-ethyl hexanoate in CCl_4 with amyl amine concentrations as shown below.

spectrum	amyl amine
15	0
16	0.001 M
17	.0025M
18	.005 M
19	.010 M
20	.025 M
21	.050 M

ABSORBANCE

0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0

350 360 370 380 390 400 425 450 475 500 525 550 575 600 650 700 750

WAVELENGTH MILLIMICRONS

APPENDIX II MATHEMATICAL RELATIONSHIPS IN COMPLEX SYSTEMS

The following mathematical relationships and definitions of terms for complex systems were taken from Bjerrum[2].

In an ideal metal amine complex system in which the maximum coordination number, N, is 4 the following reactions take place between the metal, M, and the amine, A:

$$\begin{aligned} M + A &\rightleftharpoons MA_1 \\ MA_1 + A &\rightleftharpoons MA_2 \\ MA_2 + A &\rightleftharpoons MA_3 \\ MA_3 + A &\rightleftharpoons MA_4 \end{aligned} \qquad (1)$$

The equilibrium constants for these four reactions are called consecutive or successive formation constants and are defined as:

$$\text{first formation constant:} \quad k_1 = \frac{[MA_1]}{[M][A]}$$

$$\text{second formation constant:} \quad k_2 = \frac{[MA_2]}{[MA_1][A]} \qquad (2)$$

$$\text{third formation constant:} \quad k_3 = \frac{[MA_3]}{[MA_2][A]}$$

$$\text{fourth formation constant:} \quad k_4 = \frac{[MA_4]}{[MA_3][A]}$$

The bracketed terms represent activity but can be approximated by concentration in dilute solutions.

The average number of ligands attached to the metal in a solution of a mixture of complex species is called $\bar{n}$.

$$\bar{n} = \frac{[MA_1] + 2[MA_2] + 3[MA_3] + 4[MA_4]}{[M] + [MA_1] + [MA_2] + [MA_3] + [MA_4]} \qquad (3)$$

Substitution of equations (2) in (3) gives:

$$\bar{n} = \frac{k_1[A] + 2k_1k_2[A]^2 + 3\,k_1k_2k_3[A]^3 + 4k_1k_2k_3k_4[A]^4}{1 + k_1[A] + k_1k_2[A]^2 + k_1k_2k_3[A]^3 + k_1k_2k_3k_4[A]^4} \qquad (4)$$

This function (4) relates $\bar{n}$, the average number of ligands attached to M, and A , the <u>free</u> amine concentration in solution and is called the formation function for the system. A curve that shows the relationship between $\bar{n}$ and $-\log[A]$ ($p[A]$) is called the formation curve for the system.

The degree of formation a_n for any complex species, n, is defined as:

$$a_n = \frac{[MA_n]}{C_M} \qquad (5)$$

where C_M is the total concentration of metal

Also, by definition

$$C_A = \bar{n}C_M + [A] \qquad (6)$$

where C_A is the total concentration of amine

Combining equations (2), (3), (5), and (6), an expression for a_n in terms of formation constants and free amine concentration only is obtained:

$$a_n = \frac{[A]^n \prod_{i=1}^{n} k_i}{1 + k_1[A] + k_1k_2[A]^2 + k_1k_2k_3[A]^3 + k_1k_2k_3k_4[A]^4} \qquad (7)$$

Bjerrum[2] shows that if the assumption is made that the complex MA_n has a tendency to split off a ligand proportional to n and a tendency to add a ligand proportional to N-n, the relationship between any two successive formation constants is:

$$\frac{k_n}{k_{n+1}} = \frac{(N-n+1)(n+1)}{(N-n)n}$$

or

$$k_{n+1} = \frac{(N-n)n}{(N-n+1)(n+1)} k_1 \qquad (8)$$

applying (8) to the case N=4

$$k_2 = \frac{(4-1)(1)}{(4-1+1)(1+1)} k_1 = \frac{3}{8} k_1$$

$$k_3 = \frac{(4-2)(2)}{(4-2+1)(2+1)} k_2 = \frac{4}{9}\frac{3}{8} k_1$$

$$k_4 = \frac{(4-3)(3)}{(4-3+1)(3+1)} k_3 = \frac{3}{8}\frac{4}{9}\frac{3}{8} k_1$$

and if $k_1 = 300$

$$k_2 = 112.5$$

$$k3 = 50.0$$

$$k_4 = 18.75$$

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VITA

John C. McArthur was born on February 26, 1929 in Santa Barbara, California, son of William Benton McArthur and Ardath Bertha McArthur. He entered the University of California, Santa Barbara College, in the fall of 1946, leaving the following summer to enter the University of California at Berkeley as a midshipman in the Naval Reserve Officers Training Corps. He received a B. S. Degree in Chemistry from the University of California in September 1950 and was commissioned Ensign, USN.

He served on the destroyers USS Lofberg (DD-759) and USS Cassin Young (DD-793) and with the Naval Special Weapons Unit 802 and Special Weapons Unit, Pacific, until June 1955 when he entered the United States Naval Postgraduate School at Monterey, California. He received a B. S. Degree in Ordnance Engineering from this school in June 1957. He entered Lehigh University in September 1957.